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Space Radiation Resistant Transparent Polymeric Materials

C. Giori and T. Yamauchi

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Space Radiation Resistant Transparent Polymeric Materials

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Prepared for
Langley Research Center
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SUMMARY

Many applications can be identified for a polymeric material which is highly transparent in the ultraviolet-visible region and which is stable to the vacuum-radiation environment of space. Such applications include second surface mirrors, solar cell covers, protective coatings and adhesives. A literature search in the field of ultraviolet and charged-particle irradiation of polymers has been utilized in an experimental program aimed at the development of radiation stable materials for space applications. This report presents a summary review of the literature search with a discussion of selected references. The rationale utilized for material selection and the synthesis, characterization and testing performed on several materials are described. Special consideration is given to the following basic approaches: (1) preventing energetically favored photodegradation mechanisms by appropriate structural modifications; and (2) utilizing mechanisms by which ultraviolet absorbed energy is effectively dissipated, namely, fluorescence, radiationless decay, energy transfer to acceptor molecules, and photorearrangements not involving homolytic cleavage. The feasibility of these approaches has been investigated and an experimental program aimed at verifying the applicability of these concepts to the development of ultraviolet-stable polymer structures has been initiated. Among the materials tested for ultraviolet stability in vacuum, polyethyleneoxide, polyvinylnaphthalene, and the amino resin synthesized by the condensation of o-hydroxybenzoguanamine with formaldehyde have shown promising properties. Particularly interesting, and unexpected, was the radiation behavior of poly(ethyleneoxide), in that irradiation did not cause degradation of optical properties but rather an improvement in transparency as indicated by a decrease in solar absorptance with increasing exposure time.

1. INTRODUCTION

The objective of the study presented in this report is the development, characterization and testing of high-performance polymeric materials with improved resistance to the vacuum-radiation environment of space and potentially useful in space applications such as second surface mirrors, solar cell adhesives and protective coatings.

The problem of polymer stability to a combined ultraviolet/high-energy radiation environment stems from the opposite structural requirements for stability to these two types of radiation: materials with high transparency in the ultraviolet region, such as Teflon, are stable to ultraviolet but unstable to high energy radiation. On the other hand, aromatic polymers that are capable of effectively dissipating high energy radiation through the non-localized π electrons are generally unstable to ultraviolet radiation. The work discussed in this report is aimed at achieving superior polymer stability to ultraviolet radiation, charged particle radiation (low and high energy) and combined ultraviolet-charged particle irradiation. In this study, irradiation experiments have been limited to ultraviolet exposure. Charged particle and combined irradiation tests are anticipated in a continuation of this work.

The technical approaches utilized in this work are based on the results of two previous programs conducted at IITRI for the NASA-Langley Research Center (Ref. 1,2). During these previous programs, a computerized literature search was conducted on the effects of ultraviolet and charged particle irradiation on polymers, with special consideration to the radiation damage in a space environment and to the study of the mechanisms by which absorbed ultraviolet energy can be dissipated without degradative effects. The information generated from this search was utilized for the design of an experimental program aimed at the

development of materials with improved resistance to the vacuum-radiation environment of space. Preliminary ultraviolet exposure tests indicate that the approaches selected were indeed applicable to the design of polymers with improved stability. Subsequently, a more detailed experimental program was initiated for the synthesis and evaluation of promising materials.

This report presents the following: a summary review of a literature search in the field of radiation effects; a discussion of the rationale utilized in the design of an experimental program aimed at the development of high performance materials for space applications; and a description of the synthesis, characterization and ultraviolet testing performed on the materials selected for study.

The authors wish to thank Mr. W.S. Slemp of NASA-Langley Research Center for permission to include his data in this report and for assistance in the interpretation of the results. The cooperation and assistance of Dr. N. Johnston and Dr. V. Bell of NASA-Langley Research Center is also acknowledged.

Certain commercial materials and products are identified in this paper in order to specify adequately which materials and products were investigated in the research effort. In no case does such identification imply recommendation or endorsement of the product by NASA, nor does it imply that the materials and products are necessarily the only ones or the best ones available for the purpose. In many cases equivalent materials and products are available and would probably produce equivalent results.

2. RADIATION BEHAVIOR OF POLYMERIC MATERIALS

2.1 Ultraviolet Radiation

2.1.1 Ultraviolet Absorption and Photochemical Effects

The chemical changes resulting from exposure of a polymer to ultraviolet are controlled by the two fundamental laws of photochemistry that apply to any other type of non-polymeric material. The first law (generally known as the Grotthuss-Draper Law) states that only radiations that are absorbed by the material can produce a chemical change. Most polymers contain chemical groups which absorb ultraviolet light. The carbonyl group (C=O) occurs in many polymers and may cause ultraviolet absorption up to 2500-2800Å. Aromatic compounds absorb up to 3500Å; when combined with the carbonyl group they absorb to still higher wavelength. A carbon-carbon double bond (C=C) alone absorbs below 2500Å; but when several double bonds are conjugated they absorb at increasingly higher wavelength eventually reaching the visible range.

The second fundamental law of photochemistry is generally known as the Stark-Einstein law, or law of the photochemical equivalent (Ref. 3): each molecule taking part in a photochemical reaction absorbs one quantum of the radiation causing the reaction. Since a quantum of energy is given by the product $h\nu$, according to the Stark-Einstein law the energy absorbed by a reacting molecule is also given by $h\nu$ (the product of Planck's constant and the frequency of the light absorbed).

If moles are substituted for molecules in the Stark-Einstein law, one obtains what is known as Bohr law. If the energy absorbed by a molecule is $h\nu$, the energy absorbed by a mole is given by $E=Nh\nu=Nhc/\lambda$ (where N is the Avogadro's number and c the velocity of light). Inserting the values for N, c, h, and converting ergs into kilocalories, the Bohr law is obtained (λ is expressed in Angstrom units): $E = (2.86 \times 10^5/\lambda)$ kcal/mole

The energy E for a given wavelength is usually referred to as the einstein of radiation; this is the energy of an Avogadro's number of photons, that is, the energy absorbed energy at any given wavelength. For example, for a λ = 4000Å, the einstein is 71 kcal/mole; for a λ = 2537Å (a common wavelength in photochemical work), the einstein is 113 kcal/mole, more than enough to break a carbon-carbon bond. Typical values of bond energies are shown in Table I.

The relationship between the photochemical effect of a radiation and the energy absorbed is usually expressed as quantum yield or quantum efficiency Φ:

$$\Phi = \frac{\text{number of broken bonds}}{\text{number of quanta absorbed}}$$

2.1.2 Effects of Impurities and Extraneous Materials

A ultraviolet transparent polymer must be stable to ultraviolet since there can be no damage without absorption. Unfortunately, transparency of a polymer to ultraviolet light is difficult, if not impossible, to achieve. Polyethylene and other saturated polyhydrocarbons, for example, should be inherently transparent at wavelengths higher than 2000Å. However, these polymers degrade under ultraviolet exposure, and the reason is that, to some extent, they do exhibit ultraviolet absorption. This absorption has been ascribed to impurities or structural irregularities in the polymer chains that may act as sensitizers of ultraviolet degradation. The problem of purity is very critical in the study of the photolysis of polymers. Conclusions relating polymer structure to stability can be misleading, if degradation is promoted by an unknown structural irregularity or impurity that is not typical of the polymer structure. These are sites where the degradation reaction is often initiated since the energy required is lower than that required for breaking a regular bond. It is very difficult to determine the nature of the initial absorbing species, because of their very low concentration. The formation of carbonyl groups by oxidation during polymerization or processing of polyolefins may be

Table I

BOND ENERGY TERMS FOR GENERAL USE[a]

Bond	Bond Energy Term E (K cal./mole, 25°)
C-C	82.6
C=C	145.8
C≡C	199.6
C-N	72.8
C=N	147
C≡N	212.6
C-O	85.5
C=O aldehydes	176
C=O ketones	179
C-S	65
N-N	39
N=N	100
Si-O silicones	106?[b]

[a]All values are deduced from aliphatic compounds and are taken from T.L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958, pp. 270-275.

[b]? = doubtful value

responsible for the initial absorption and could initiate photolytic degradation (Ref. 4, 5). It has been reported (Ref. 6) that aromatic impurities such as phenanthrene, anthracene and naphthalene are present in polyethylene and act as sensitizers of ultraviolet degradation. The use of model compounds in the study of polymer photolysis has the very important advantage that the study is conducted on pure materials.

2.1.3 Relationship Between Absorption and Stability

Although ultraviolet instability is undoubtedly related to ultraviolet absorption, the relationship between transparency and stability is not simple to predict. For example, traces of keto groups in polyethylene make the polymer very sensitive to ultraviolet light, whereas poly(methylmethacrylate) with one keto group for each repeating unit is among the polymers with the highest ultraviolet stability. It appears that some polymer structures, unlike others, have a mechanism for dissipating absorbed energy that otherwise would cause breakdown of the chain. Absorbed energy can be dissipated as heat or re-radiated at longer wavelength. A better understanding of these phenomena would probably explain why the same absorbing group may have a negative effect on ultraviolet stability in a certain polymer structure and be relatively harmless in another structure.

An interesting question is whether the effect of ultraviolet radiation on polymers can be predicted on the basis of a knowledge of the effect of gamma or other ionizing radiation. A few studies have been concerned with comparing the effect of ultraviolet and gamma radiation on polymers. Charlesby

has demonstrated for poly(methylmethacrylate) (Ref. 7) that the degradation process due to ionizing and ultraviolet irradiation is the same; only the efficiency of the two processes differ, since the energy absorbed per main chain cleavage is about 550 eV with ultraviolet radiation and about 65 eV with gamma radiation. A part from this difference in efficiency, Charlesby concludes that the two reactions are very similar and result in the formation of similar free radicals, as seen by EPR. (It must be noted that "ionizing" radiations do not normally produce ionization in organic polymers, and the observed effects are generally explained in terms of free radical reactions with no participation of ionic species). In a following paper, however, Charlesby (Ref. 8) points out an important difference between gamma and ultraviolet irradiation of poly-(methylmethacrylate): the susceptibility of an ester group in polymethylmethacrylate to undergo homolysis by ultraviolet radiation is about 40 times that with gamma radiation, when compared to the susceptibility of the main chain. This pronounced difference is ascribed to the fact that while gamma radiation is absorbed at random by the polymer chain, absorption of ultraviolet is selective at the keto group of the ester link. It may be concluded that the selective absorption of ultraviolet light is responsible for the different effect of ultraviolet and gamma radiation. This consideration is certainly applicable to polymer structures other than poly(methylmethacrylate).

It is interesting to note that some high-temperature aromatic polymers that are highly stable to gamma-radiation, such as the polyarylsulfones, are very unstable to ultraviolet radiation (ref. 9, 10, 11). This behavior is often observed with aromatic structures exhibiting high absorption in the ultraviolet region.

A few studies have appeared on the wavelength dependence of photodegradation in organic polymers. As a general rule, the lower the wavelength of the radiation absorbed the greater is the damage (ref. 12). However, it has been found that, in the case of aromatic polyamides, the most damaging radiation lies in the near ultraviolet region (ref. 13). The reason for this unusual behavior is not explained. It is difficult to see how a less energetic ultraviolet radiation could cause more damage than a shorter, more energetic radiation that is equally absorbed by the polymer.

2.1.4 Physicochemical Aspects of Polymer Photolysis

It is important to consider the various events that may follow absorption of a photon by a certain group in a polymer molecule. Most organic molecules lie in a singlet ground state. Absorption of a photon raises the molecule to an excited singlet or triplet state. If the molecule has sufficient energy in the excited state, whether it be singlet or triplet, bond dissociation may take place. This bond-breaking process is relatively slow and is statistically more probable in the long-lived triplet state. If a C-H bond is broken, the process of excitation and decomposition can be represented as follows:

$$RH \xrightarrow{h\nu} RH^*$$

$$RH^* \longrightarrow R\cdot + H\cdot$$

This decomposition process must compete with other deexcitation processes. The excited molecule may revert to the ground state by radiationless transitions and the emission of heat. Reversion to the ground state may also be accomplished by photon emission; the excited molecule re-radiates part of the energy at a longer wavelength as the electron returns to the ground state. This phenomenon is known as fluorescence or phosphorescence, depending on whether the excited state is a singlet or a triplet, and whether or not there is a time lag in the re-radiation process. These harmless deexcitation processes allow the excited molecule to return to the ground state without producing a chemical change.

$$RH^* \longrightarrow RH + \text{heat}$$

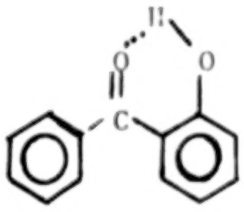
$$RH^* \dashrightarrow RH + h\nu$$

Reversion to the ground state may also be accomplished by transfer of electronic energy to another group in the vicinity of the excited molecule:

$$M_1^* + M_2 \longrightarrow M_1 + M_2^*$$

Such electronic energy transfer is believed to play an important role in polymer photodegradation, particularly where long-lived triplet states are involved (ref. 14). The importance of energy transfer processes becomes apparent if one considers that photolytic degradation is not entirely a consequence of absorption of a photon by the particular group undergoing degradation. Very often energy is transfered to this "weak" group from a different absorbing group in the polymer or from an absorbing impurity. Some workers have devoted considerable attention to the study of polymer photolysis in the presence of "sensitizing" impurities, such as the photolysis of silicones in the presence of naphthalene (ref. 15) or the photolysis of polypropylene in

the presence of phenanthrene (ref. 16). Electronic energy transfer is involved in the sensitized degradation process. An interesting case of intramolecular energy transfer is the photolysis of polymethylphenylsiloxane (ref. 17), in which photodegradation occurs predominantly at the methyl group, although the phenyl group is responsible for absorption. It is interesting at this point to observe the similarity between a "stabilizer" and a "sensitizer" of ultraviolet degradation. Both molecules are strong ultraviolet absorbers and will reach an excited state as a result of photon absorption. The "sensitizer" will return to the ground state by transfer of energy to the polymer, therefore initiating degradation. The stabilizer will return to the ground state by re-radiating the absorbed energy as heat or as a photon of longer wavelength. For a stabilizer to be effective it is essential that the energy of excitation be dissipated quickly. Since transfer of energy to the polymer is a competitive process, the rate of deexcitation is very critical. It is interesting to observe that while benzophenone is a sensitizer of photochemical reactions and is quite reactive in its excited state, o-hydroxy benzophenone is very stable to ultraviolet, and is in fact used as ultraviolet stabilizer. There is substantial evidence that the reason for the stability of o-hydroxybenzophenone is the ability of the photoexcited molecule to return to the ground state through a radiationless transition so that the energy is given up in the form of harmless heat (ref. 22,23). This behavior is undoubtedly associated with the capability of the o-hydroxybenzophenone to form an intramolecular six-membered hydrogen-bonded ring:



The excited state induced by absorption of a quantum of light is deactivated through a reversible mechanism that leaves the stabilizer molecule unchanged and does not cause any chemical effect in the polymer.

Recently it has been demonstrated that compounds that do not absorb the incident radiation can also stabilize the polymer by abstraction of the excited state energy from the polymer molecule. Guillet refers to these types of compounds as "quenchers" (ref. 18). Heskins and Guillet (ref. 19) have shown that 1,3-cyclooctadiene can quench the excited triplet state in polyvinylketones and ethylene-carbon monoxide copolymers and stabilize these polymers against photodegradation. There is strong evidence that the mechanism of action of nickel chelates of thiobisphenols (ref. 20), that are known to be good stabilizers for polyolefins, involves primarily an energy transfer mechansim. The stabilizing effect of pyrene and p-terphenyl in poly(methylmethacrylate) was also interpreted in terms of an energy transfer mechanism (ref. 21).

2.2 Charged Particle and High Energy Electromagnetic Radiation

The effects of radiation on polymers have been reviewed in several books (ref. 24-30) and articles (ref. 31, 32). Also a survey of the patent literature with reference to the use of radiation methods in plastic technology is available (ref. 33) and a review of the technology of radiation processing has been published (ref. 34). In these reviews, the effect of radiation is discussed primarily in terms of utilization of the radiation for the improvement of specific plastic properties by cross-linking.

The effects of many types of high-energy radiation on polymers have been described, including electromagnetic radiation (X-rays, gamma rays), and particulate radiation (electrons, protons and neutrons). Although X-rays and gamma rays are similar to ultraviolet radiation in being electromagnetic radiations, their quanta are associated with much higher energies. While the quanta of ultraviolet radiation have energies in the range 50-1000 kcal, particulate and high-energy electromagnetic radiations may have energies up to 10^8-10^9 kcal, more than enough to displace electrons from organic compounds.

The absorption of ultraviolet irradiation occurs at specific groups, and produces electronic excitation that may lead to dissociation into radicals. The absorption of charged particles or high-energy quanta is non-specific with respect to chemical structure, and may result in the displacement of electrons with formation of ion-radicals:

$$A \rightarrow A.^{\oplus} + e^{-}$$

The electron produced can have sufficient energy to leave the zone of primary ionization, and may produce ionization or excitation along the course of its trajectory.

It is important to note that, while displacement of electrons with production of ion-radicals is the primary effect of high energy radiation, the reactions promoted by the radiation generally involve free radical mechanisms rather than ionic mechanisms. An interesting demonstration was given by Tobolsky (ref. 35) who showed that on irradiation with beta rays a styrenmethylmethacrylate mixture, the copolymer obtained was the type expected for a free radical initiated polymerization. Ionic initiation would have produced almost pure homopolymers.

There are several ways by which free radicals can form from the primary products of radiation; generally, an excited molecule is formed, which can be either in a singlet or triplet state. This can be formed by recombination of the ion-radical and electron:

$$A \rightarrow A.^{\oplus} + e^{-} \rightarrow A^{*}$$

Another possibility is the recombination of the electron with another molecule to form a negative ion which then combines with a positive ion:

$$A \rightarrow A.^{\oplus} + e^{-}$$

$$B + e^{-} \rightarrow B.^{\ominus}$$

$$A.^{\oplus} + B.^{\ominus} \rightarrow A^{*} + B^{*}$$

Formation of free radicals results from the decomposition of the excited molecule, e.g.:

$$(R\text{-}R')^{*} \rightarrow R. + R'.$$

$$(R\text{-}H)^{*} \rightarrow R. + H.$$

The picture is further complicated because the ions or radicals themselves may be in an excited state, and produce different decomposition products. The important point that must be emphasized is that the lifetime of the ions produced by electron displacement is extremely short, consequently, ionic reactions seldom occur as a result of irradiation.

Chapiro (ref. 27) classified polymers in two general groups depending on whether the predominant effect of radiation was cross-linking or chain scission (Table II). However, it should be noted that these two effects are often concurrent and competitive, therefore, clear-cut classifications are impossible. As a general rule, vinyl polymers possessing tertiary carbon atoms in the main chain cross-link as a result of irradiation, whereas vinyl polymers possessing quaternary carbon atoms in the main chain undergo chain scission. This effect is demonstrated by comparing the radiation behavior of polystyrene with polymethylstyrene, and polymethylacrylate with polymethylmethacrylate. This effect is similar to the one already discussed in the case of ultraviolet irradiation (ref. 1); the lower reactivity of free radicals derived from quaternary carbon atoms was proposed to explain this behavior.

In general, vinyl monomers that have high monomer yields in thermal degradation will degrade by chain-scission upon irradiation, whereas those with low monomers yields will cross-link rather than degrade (ref. 36, 37). The degrading polymers are also those whose monomers have relatively low heats of polymerization (ref. 38). In addition to the structures with regularly recurring quaternary carbons, the fully halogenated structures (e.g., polytetrafluoroethylene, polychlorotrifluoroethylene) and the polymers with high oxygen content (polyoxymethylene, cellulose) undergo predominant chain-scission by irradiation.

Optical instability (i.e., discoloration) is the most important aspect of radiation damage in thermal control materials for space applications. Production of color is usually ascribed to the formation of multiple conjugated unsaturation or it may be the result of a high concentration of free radicals trapped in the polymer structure.

Table II

Crosslinking and Degradation in Irradiated Polymers (Ref. 27)

Crosslinking Polymers	Degrading Polymers
Polymethylene (polyethylene)	Polyisobutylene
Polypropylene	Poly(α-methylstyrene)
Polystyrene	Polymethacrylates
Polyacrylates	Polymethacrylamide
Polyacrylamide	Poly(vinylidene chloride)
Poly(vinyl chloride)	Cellulose and derivatives
Polyamides	Polytetrafluorethylene
Polyesters	Polychlorotrifluoroethylene
Polyvinylpyrrolidone	
Rubbers	
Polysiloxanes	
Poly(vinyl alcohol)	
Polyacrolein	

Formation of volatile by-products is an important phenomenon associated with radiation damage. Most cross-linking polymers, such as polyethylene, polystyrene and polyvinylalcohol, produce hydrogen as the only significant by-product of irradiation, suggesting that cross-linking takes place mainly by elimination of hydrogen between adjacent chains. Degrading polymers generate complex mixtures of volatile by-products whose composition is markedly dependent upon the polymer chemical structure.

As a general rule, polymers containing phenyl groups, either in the main chain or as pendant groups, are more resistant to high-energy radiation than aliphatic polymers. The greater stability is due to the resonance energy of the aromatic structure. Energy from radiation is preferentially absorbed and dissipated by the non-localized π electrons. Therefore, the materials having the greater resonance energy have the greater stability towards radiation.

Chapiro (ref. 27) classified various commercial plastics into twelve groups according to their resistance to radiation damage. As expected, the most radiation resistant polymers contain aromatic substituents. Polymers such as Teflon and PMMA, that degrade by chain-scission, are the least stable. In the complete absence of oxygen, however, Teflon exhibits better resistance to radiation damage (ref. 39). Elastomers are also very susceptible to radiation damage. Most rubbers lose their elastic properties for doses of the order of the order of 10^2 rads (Ref. 27). This effect is particularly pronounced in the presence of oxygen. It has been found that phenyl and other aromatic groups are not only able to dissipate excitation energy without decomposing, but are able to accept energy from alkyl groups, thereby protecting them. This behavior is opposite to the one observed in the case of ultraviolet irradiation.

3. LITERATURE RETRIEVAL

During a previous program, contract No. NAS1-12549, a literature search was conducted on the effects of ultraviolet irradiation on polymeric materials, with particular emphasis on vacuum photolysis, mechanisms of degradation and energy transfer phenomena (Ref. 1). During a subsequent program, contract No. NAS1-12549, the literature search was expanded by including the effects of charged particles and high energy electromagnetic radiation on polymers, with special consideration to radiation damage in a space environment (Ref. 2). The procedures employed by IITRI's Computer Search Center and the keywords categories utilized for the search were discussed in previous reports (Ref. 1, 2). Table III presents a summary of the sources utilized for the search.

TABLE III

LITERATURE RETRIEVAL SOURCES

1. IITRI

   1.1 Computer Search

      Chemical Abstr. (1969-present)
      NTIS (1967-1974)

   1.2 Manual Search

      Chemical Abstr. (1958-1969)

2. Outside Sources

   2.1 DDC

   2.2 N.C. Res. Triangle Park (NASA Files, Star, IAA)

   2.3 Rad. Chem. Data Center, University of Notre Dame

3.1 Ultraviolet radiation effects

In this section, some important classes of polymeric materials are reviewed with a brief discussion of their photolytic behavior. It should be noted that because of proprietary interests, much of the literature pertaining to polymer photochemistry does not appear in scientific journals. Much of the data on photostabilization, for instance, is to be found in the patent literature. The publications reviewed here are the ones which have the greatest scientific merit and the ones that deal more specifically with the mechanisms of photolysis. Particular consideration has been given to studies dealing with photolysis in vacuum, although some studies performed in air have been included, depending upon their technical relevance, and whether or not any study performed in vacuum was available on that particular polymer.

3.1.1 Polyethylene

A pure polyethylene chain should not absorb radiations of wavelength higher than 2000Å. In reality, polyethylene does absorb in the ultraviolet due to impurities or irregularities in the polymer chain. Since impurities and irregularities may vary with the sample and the source of the polymer, the interpretation of the results and the comparison of data of different authors is particularly difficult. The formation of carbonyl groups as a result of oxidation during polymerization or processing is often blamed for ultraviolet absorption and consequent instability of polyethylene. Charlesby and Partridge (ref. 4.5) have shown that carbonyl groups are indeed present in polyethylene and that the ultraviolet and gamma induced thermoluminescence and phosphorescence of polyethylene are associated with the presence of carbonyl impurities.

Polyethylene undergoes much faster physical change upon irradation in air than in nitrogen (ref.40). Charlesby (ref. 41) exposed Polyethylene to 2537Å radiation both in oxygen and in nitrogen; he found that ultraviolet exposure results in an increased absorbance in the 2000-2800Å region, and ascribed the absorbtion to conjugated

unsaturation. Cotten (ref. 42) showed that both chain-scission and cross-linking take place on irradiation of polyethylene in air, and that scission is favored in the highly crystalline region. Since the diffusion rate of oxygen into amorphous region. Since the diffusion rate of oxygen into amorphorus regions is greater than in crystalline regions, cross-linking occurs preferentially in the amorphous regions (ref. 43). Ohnishi (ref. 44) irradiated polyethylene in vacuum with electrons at - 78°C and by EPR, found allyl radicals; these allyl radicals are converted to alkyl radicals under 2537Å irradiation. The total radical concentration does not change, indicating the existence of an alkyl-allyl equilibrium:

$$-CH_2-CH-CH=CH- \rightleftharpoons -CH-CH_2-CH=CH-$$

Pivovarov (ref. 6) reported that polyethylene always contains phenanthrene, anthracene and naphthalene as impurities, and that these aromatic compounds act as sensitizers of ultraviolet degradation.

3.1.2 Polypropylene

Several free radical species have been detected by Yoshida (ref. 45) and Browning (reg. 46) in the EPR spectrum of irradiated polypropylene:

$$\begin{array}{ll} CH_3 & -CH_2-CH-CH_2- \\ -CH_2-CH-CH_2- & -CH-CH-CH- \\ \quad\quad CH_2 & \quad\quad CH_3 \quad CH_3 \end{array}$$

Milinchuk (ref. 47) has observed the same type of allyl-alkyl free radical equilibrium described for polyethylene in the ultraviolet irradiation of polypropylene in the absence of air. In the presence of air, peroxy radicals derived from both the allyl and alkyl radical are formed. Klinshport (ref. 48) finds that the transformation is reversible and in the dark the alkyl radical is transformed into allyl radical. Malinskaya (ref. 16) has studied the photolysis of polypropylene containing phenanthrene as sensitizer. He found by EPR the same radicals described by Yoshida and Browning; he suggests that the samples studied by these workers contained undetected amounts of aromatic impurities. McTigue (ref. 49) reported that pigments are beneficial for ultraviolet stability of polypropylene and that carbon black is the most effective.

3.1.3 Unsaturated Polyhydrocarbons

A paper by Golub (ref. 50) reviews the photolysis in vacuum of the following unsaturated polymers:

1,4 polyisoprene: $-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-$

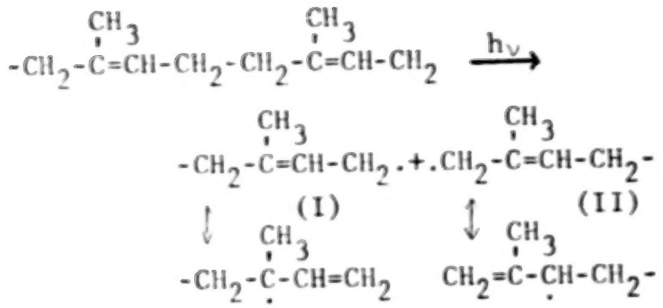
1,4 Polybutadiene: $-CH_2-CH=CH-CH_2-$

1,2 polybutadiene: $-\underset{CH=CH_2}{\underset{|}{CH}}-CH_2-$

3,4 Polyisoprene: $-\underset{C=CH_2}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH-CH_2-$

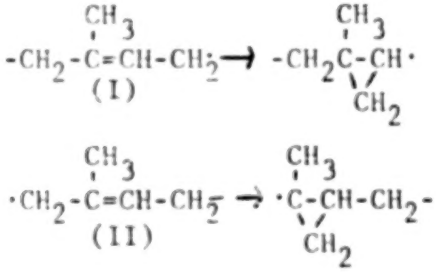
These polymers were found to undergo a radiation induced cis-trans isomerization.

In the irradiation of 1,4 polyisoprene and 1,4 polybutadiene, the energy absorbed by the double bond is diverted into breaking C-C bonds connecting the repeating units:

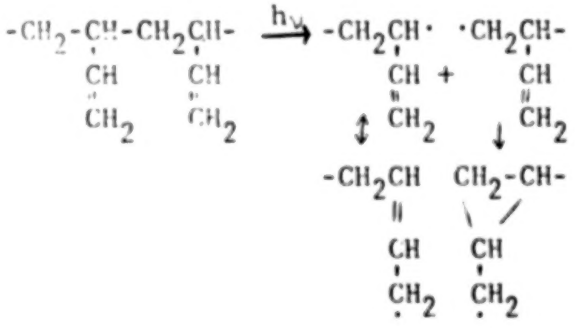


The C-C bond connecting the repeating units is the weakest bond in the chain, with a strength (55 kcal/mole) which is lowered from the normal C-C bond strength by the resonance energy of the two allyl radicals formed on chain scission.

The formation of cyclopropyl groups during photolysis is explained as follows:



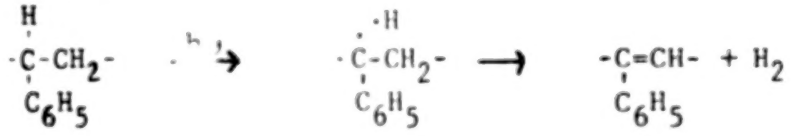
With 1,2-polybutadiene and 3,4-polyisoprene a similar process of chain cleavage takes place:



Cyclopropyl group formation takes place by a process similar to the one shown for 1,4-polyisoprene.

3.1.4 Polystyrene

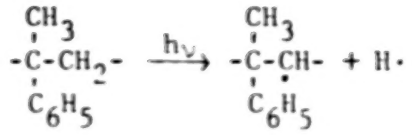
In spite of the large amount of literature on the photolysis of polystyrene, only two studies, one by Fox (ref. 51) the other by Grassie (ref. 52), deal with the mechanisms of photolysis in vacuum. These workers exposed films of polystyrene to 2537Å radiation in vacuum. They found that ultraviolet radiation causes almost exclusively cross-linking. Chain scission was negligible, unless oxygen was present. Yellowing was very pronounced, even in the absence of oxygen. Grassie suggests that color is due to conjugated unsaturation, and he points out that on melting a degraded film that was yellow the color of the melt turns immediately black. He indicates that the photolytic process that is energetically more favorable involves removal of the hydrogen atom from the tertiary carbon:



Cross-linking results from recombination of the tertiary radicals formed by hydrogen abstraction. As a general rule, the more reactive the removed hydrogen, the less reactive the resulting free radical; therefore, cross-linking occurs. Alternately, the less reactive the hydrogen, the more reactive the new free radical, and chain scission becomes the predominant reaction.

3.1.5 Poly(α-methylstyrene)

Substitution of a methyl group for the α-hydrogen in polystyrene results in a structure that degrades in a totally different way. In polystyrene, the photolysis involves exclusively cross-linking, whereas in poly(α-methylstyrene) photolysis involves exclusively chain scission:



The reason for the different behavior is due to the fact that a relatively stable tertiary radical is formed with polystyrene while an unstable secondary radical is the precursor to the more rapid chain scission occurring in poly(α-methylstyrene). The less stable the radicals, the more likely are they to decompose rather than to combine to give cross-links (ref. 53).

Stokes and Fox (ref. 54) have studied the photolysis of poly(α-methylstyrene) films in vacuum. Monomer is formed by depolymerization and the monomer yield increases with increasing temperature. At 27°C, the quantum yield for random scission was 10^{-3} and for monomer formation 7×10^{-3} (approximately 7 monomer units for each scission). At 155°C, the quantum yield for scission was 2×10^{-2} and for monomer formation 0.5 (approximately 25 monomer units for each scission).

3.1.6 Fluorocarbon Polymers

Many papers have been published on the effects of gamma irradiation on fluorocarbon polymers, but very little has been published on ultraviolet irradiation. Bowers (ref. 55) studied the cross-linking of fluoropolymers by irradiation at elevated temperatures. The source used was a quartz mercury lamp, emitting radiation principally at 1849 and 2536Å. Under nitrogen, ultraviolet irradiation of poly(chlorotrifluoroethylene) at 250°C resulted in degradation while only minor degradation was observed with poly(tetrafluoroethylene) at 325°C; no cross-linking was noted. With Teflon 100 FEP (a copolymer of tetrafluoroethylene and hexafluoropropene) both scission and cross-linking occur and the latter increases with increasing temperature.

Stephenson (ref. 56) studied the photolysis of polytetrafluoroethylene both in nitrogen and vacuum. Unlike other polymers, the drop in tensile strength and elongation by irradiation

with 2537Å ultraviolet light is more rapid in vacuum than in nitrogen. A study of the wavelength dependence of photodegradation of poly(tetrafluoroethylene) showed that the efficiency in producing degradation increases with decreasing wavelength (ref. 56). A study of the absorption spectrum of polytetrafluoroethylene (as well as of other unfluorinated polyhydrocarbons with no natural absorption in the ultraviolet) showed that polymer absorption and luminescence in the UV range are due to aromatic impurities (ref. 6).

3.1.7 Poly(methylmethacrylate)

The photolysis of poly(methylmethacrylate) has been studied in great depth by several workers. The photolytic process is very similar to poly(α-methylstyrene), in that the polymer undergoes random chain cleavage with no cross-linking. Photodegradation at room temperature produces small amounts of volatile materials, but the formation of monomer by "unzipping" increases with increasing temperature.

Fox (ref. 12) points out that because of the low absorption coefficient of poly(methylmethacrylate) at 2537Å, this radiation can penetrate a thin film with only slight attenuation, whereas with more highly absorbing polymers a "skin" effect is produced. The photolysis of poly(methylmethacrylate) was studied in vacuum at 25°C with a medium pressure mercury lamp. The quantum yield for random scission is 4×10^{-2}. Methyl formate, methanol and methylacrylate are formed in quantum yields of 0.14, 0.48 and 0.20, respectively, indicating a depolymerization of about five monomer units for chain break (ref. 57).

Charlesby and Thomas (ref. 7) studied the photolysis in vacuum, air and nitrogen. Surprisingly, the quantum yields in air or nitrogen are lower than in vacuum. Fox (ref. 12) points out that oxygen might act as an inhibitor by scavenging secondary polymer radicals which are precursors to chain scission. While nitrogen might suppress the diffusion of gases from the film, it is difficult to see how this could affect the rate of scission.

Many workers have noted the appearance of a new band at 2850Å in ultraviolet irradiated poly(methylmethacrylate). This new band appears by irradiation either in air or vacuum, and remains with the polymer even after reprecipitation, indicating that the absorbing group is part of the chain (ref. 57). Fox (ref. 57) ascribes the 2850Å absorption to a carbonyl chromophore formed by secondary reactions after homolysis of the ester. Frolova (ref. 58) ascribes it to conjugated unsaturation in the chain, because the absorption shifts to higher wavelengths during irradiation. He supports this conclusion with a study of the IR spectrum of the irradiated polymer that shows new bands at 1615 and 1640cm^{-1} indicative of the presence of olefinic unsaturation.

Electron spin resonance spectra of ultraviolet and gamma irradiated poly(methylmethacrylate) are identical, indicating that the same free radicals are present in the irradiated polymers (ref. 59,7).

3.1.8 Poly(methylacrylate)

A study by Fox (ref. 60) indicates the formation of a weak band at 2800Å on irradiation in vacuum at 2537Å. The main volatile products are formaldelyde, methanol and methylformate (from ester group decomposition), along with CO_2 and hydrogen. The rate of CO_2 formation increases with dose; since the end-group concentration increases with dose, it is suggested that CO_2 comes from the terminal end groups.

3.1.9 Poly(ethylacrylate)

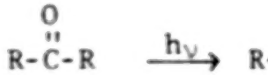
A study by Jacobs (ref. 61,62) shows that both cross-linking and chain scission take place during irradiation. The time necessary to produce insoluble gels increases with decreasing temperature. Below the glass transition temperature (-17°C) there

is no formation of insoluble products. It appears that when the mobility of the chain is reduced, the recombination of radicals to give cross-links is less likely to occur.

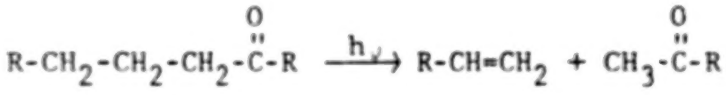
3.1.10 Polyketones

The study of the photolysis of polyketones is particularly interesting because the photolysis of simple aliphatic ketones is a well understood process. Two primary reactions are known to occur in the photolysis of aliphatic ketones:

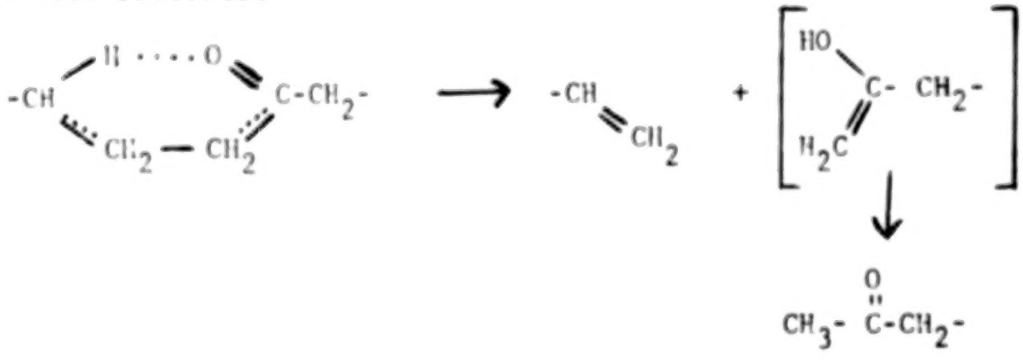
Norrish Type I:



Norrish Type II:

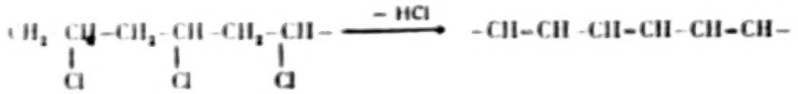


Wissbrun (ref. 63) studied the photolysis of poly(methylvinylketone) at 3130Å. An increased absorption below 2500Å was observed, and acetaldehyde, carbon monoxide and methane were formed in quantum yields of 0.06, 0.003, and 0.0006 at 80°C. Guillet (ref. 64) studied the photolysis of poly(methylvinylketone) and polyethylene-carbon monoxide copolymer. He finds that the photolysis of polyketones is described very well by the Norrish type I and II. It is interesting to note that the Norrish type II follows a molecular mechanism that does not involve formation of free radicals:



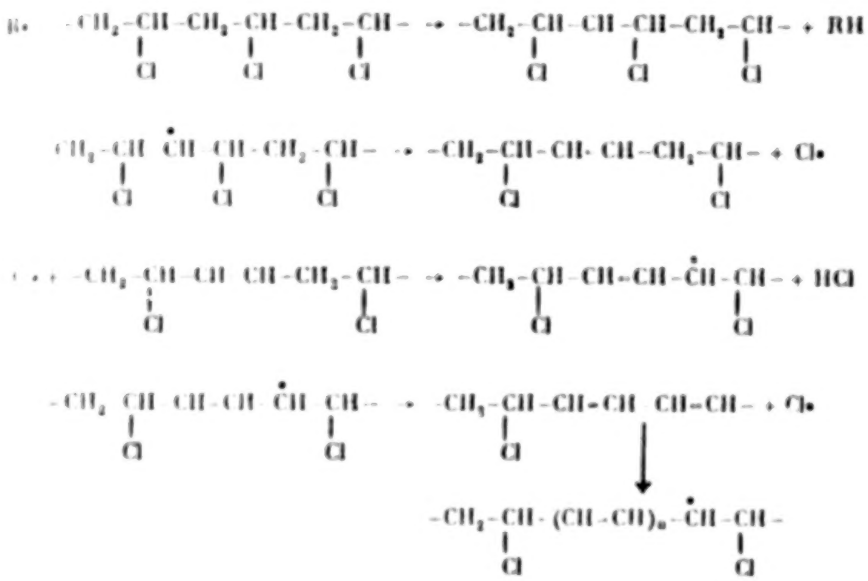
3.1.11 Polyvinylchloride

The spectroscopic changes produced by ultraviolet irradiation in vacuum of PVC films have been studied by Golub (ref. 65). The main photolytic effect is the formation of a conjugated polyene system through progressive loss of HCl:



As the sequence of conjugated double bonds increases, absorption increases progressively from the ultraviolet to the visible portion of the spectrum. Consequently, PVC films become increasingly colored on irradiation. The quantum yield for HCl formation is independent of wavelength below 3400A, which is the effective photochemical cut-off wavelength.

The following free-radical mechanism has been proposed for the dehydrochlorination reaction:

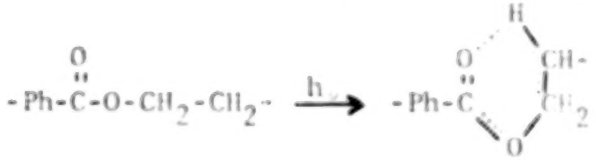


3.1.12 Polyacrylonitrile

Jellinek (ref. 66) reported that exposure of polyacrylonitrile to 2537Å irradiation in vacuum results in cross-linking and formation of HCN. Fox (ref. 12) points out that the longest wavelength absorption maximum of the nitrile group is about 1600Å. Polyacrylonitrile should therefore, be very transparent to ultraviolet. However, absorption occurs with a maximum at 2650Å that is somehow associated with the polymer structure itself. The chromophore causing the absorption has not been identified.

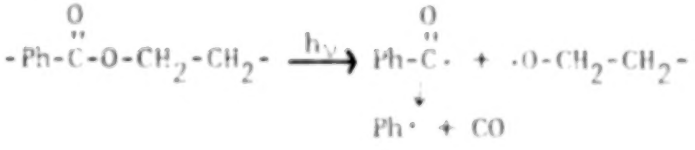
3.1.13 Polyesters

Three recent papers have been published by Day and Wiles on the photolysis of poly(ethyleneterephthalate) in nitrogen and air (ref. 67, 68, 69). As a result of irradiation, an increase in carboxyl groups was observed, that was ascribed to the decomposition of the ester group by a Norrish Type II process:

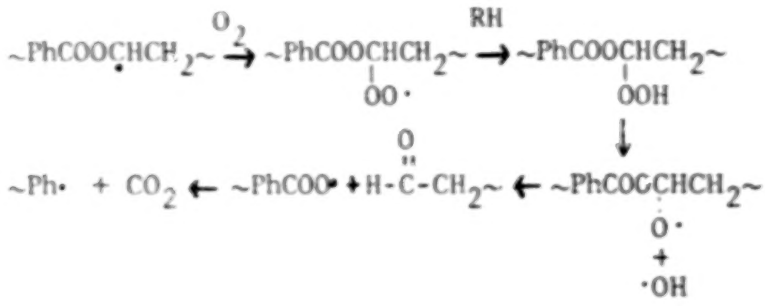


$$-Ph-COOH + CH_2=CH-$$

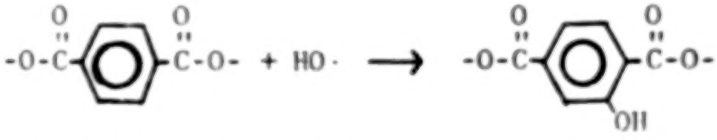
They found that CO and CO_2 were the major volatile products and that CO_2 was formed primarily in the presence of air. The formation of CO was explained on the basis of a Norrish Type I cleavage reaction:



The fact that CO_2 formation takes place primarily in the presence of oxygen suggests that hydroperoxidation is involved:

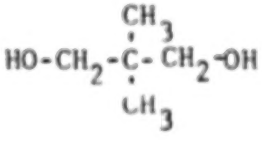


Another phenomenon observed in poly(ethyleneterephthalate) irradiated in the presence of air is the appearance of a fluorescent band at 4600A This band was ascribed to the formation of an hydroxylated derivative resulting from the attack of the OH radical (formed from the reaction above) on the phenyl ring:

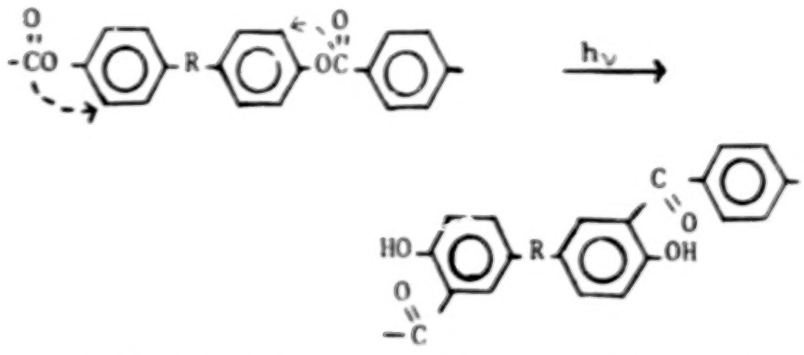


The nature of the fluorescent product was confirmed by Pacifici (ref. 70) who compared the fluorescence spectrum of irradiated poly(ethyleneterephthalate) with that of synthetic hydroxylated polyesters.

It has been reported (ref. 71) that polyester compositions based on neopentylglycol exhibit superior ultraviolet resistance. This is probably due to the fact that the cleavage of the ester via Norrish Type II cannot occur because of the absence of hydrogen on the carbon atom β to the hydroxyl groups in neopentylglycol:



A paper by Cohen (ref. 72) describes a number of aromatic polyesters that under ultraviolet irradiation rearrange to an o-hydroxybenzophenone structure according to the photo-Fries reaction:



These polyesters are reported to be useful as coatings for protecting substrates ordinarily sensitive to ultraviolet light.

3.1.14 Polyamides

A paper by Moore (ref. 73) deals with the photolysis of Nylon 66 and of model N-alkyl amides both in nitrogen and air. Both crosslinking and chain scission were found to occur. The mechanisms proposed are basically in agreement with the mechanisms proposed previously by Rafikov (ref. 74). The mechanism for cross-linking involves elimination of an hydrogen atom from the carbon adjacent to the nitrogen atom followed by combination of two radicals:

$$-CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2- \xrightarrow{h\nu} -CH_2-\overset{O}{\overset{\|}{C}}-NH-\underset{\downarrow}{\overset{\cdot}{C}}H-CH_2- + H\cdot$$

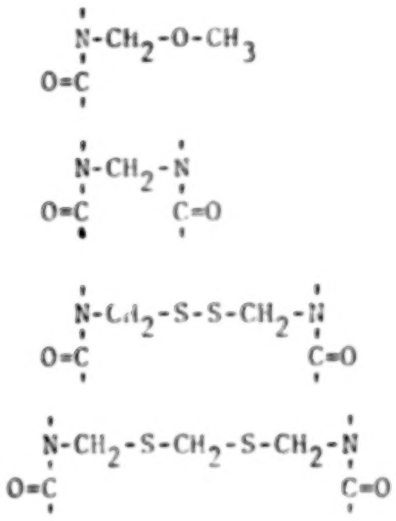
Cross-linking

The mechanism for chain scission involves cleavage of C-N bonds with subsequent formation of CO and ethylene:

$$-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2- \xrightarrow{h\nu} -(CH_2)_3-\overset{O}{\overset{\|}{C}}\cdot + \cdot NH-CH_2-$$

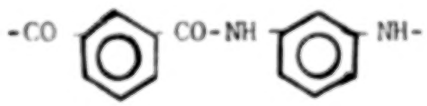
$$-CH_2\cdot + CH_2=CH_2 \longleftarrow -CH_2-CH_2-\underset{\downarrow}{CH_2}\cdot + CO$$

Brick (ref. 75,76) reported some structural modifications of Nylon 6 that produce a fiber crimping effect. The following Nylon 6 modifications were considered:

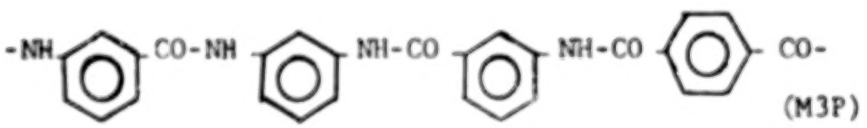


These structures were reported to possess good ultraviolet stability (with the exception of the disulfide). Comparative data with the ultraviolet stability of unmodified Nylon 6 were not given.

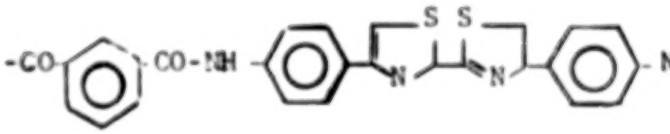
A paper by Johnson (ref. 13) discusses the photodegradation of three aromatic polyamides:



(NOMEX) (1)



(M3P) (2)



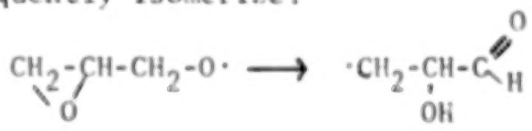
(BTA) (3)

A study of the wavelength dependence of photodegradation shows that all three polymers are degraded by light of much longer wavelength than that which is harmful to other polymers. Polymer (1) and (2) show degradation maxima at 3600 and 3700Å; polymer (3) is degraded significantly even by visible light (particularly 4140Å). The mechanism of degradation is not known.

A study by Krasny (ref. 77) on the photostabilization of Nomex fibers confirms that Nomex is particularly sensitive to photodegradation in the wavelength region of 3600-3900Å. Ultraviolet stabilizers exhibiting strong absorption in this critical wavelength region were found to be unsatisfactory because of polymer incompatibility or other undesirable effects.

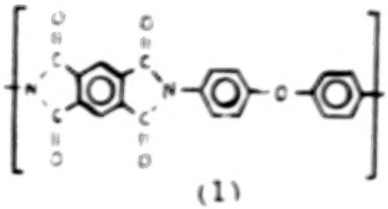
3.1.15 Polyethers

Kelleher (ref. 78) studied the photoxidation of poly(oxymethylene) and found that random chain scission occurs followed by extensive depolymerization to formaldehyde. A similar process occurred in a oxyethylene-oxymethylene copolymer, except that depolymerization appeared to stop at the ethylene unit. Grassie (ref. 79) studied the photoxidation of poly(oxymethylene) at 2537 and 3650Å. Hydrogen and carbon monoxide were the main decomposition products. Irradiation in air produced well defined changes in the hydroxyl and carbonyl regions of the infrared spectrum. Irradiation at 2537Å was approximately 100 times more effective than 3650Å irradiation. Sukhareva (ref. 80) studied the spectra of ultraviolet irradiated epoxy coatings and observed the appearance of a band with a frequency of 1685cm^{-1} that was ascribed to the carbonyl group. Carbonyl group formation takes place by a radical mechanism of epoxy decomposition at the terminal groups, leading to the formation of free radicals that can subsequently isomerize:

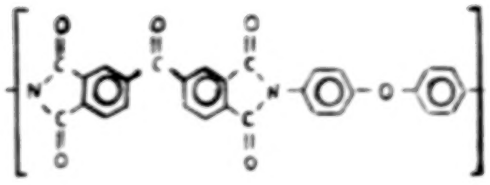


3.1.16 Polyimides and Polyamide-imides

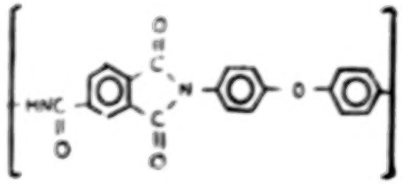
Alvino (ref. 61) studied the ultraviolet stability of the following polyimides and polyamide-imide:



(1)



(2)

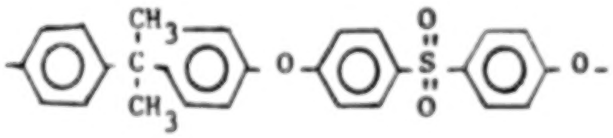


(3)

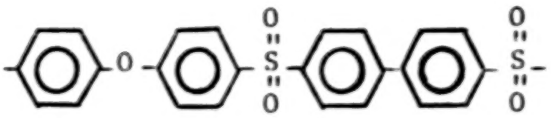
He found that these polymers were sensitive to ultraviolet light, especially in the presence of moisture. the mechanical and electrical properties of (3) deteriorated more rapidly than those of (1) and (2) under both wet and dry conditions. The increase in deterioration rate on going from dry to wet environment was much greater for (1) and (2) than for (3), indicating that (3) had greater hydrolytic resistance. The electrical properties of (1) and (2) were unaffected by ≤ 6000hr irradiation in a dry environment.

3.1.17 Polysulfones

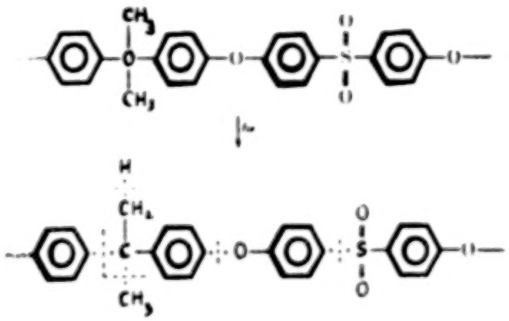
Aromatic polysulfones have been reported to possess outstanding resistance to high energy radiation (ref. 9). Their ultraviolet stability, however, is very poor. Poor ultraviolet stability has been reported for the Union Carbide polysulfone (ref. 10):



and for the 3M polysulfone ("Astrel" 360) (ref. 8):



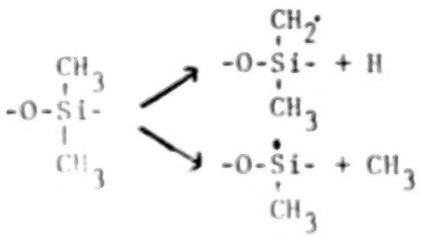
The work of Gesner and Kelleher (ref.10) provides a good description of the photo-oxidative behavior of the Union Carbide polysulfone, which is consistent with a random chain scission mechanism. In the initation process, scission apparently takes place at every bond except the aromatic C-C and C-H bonds:



The work of Alvino (ref.11) on 3M polysulfone shows some interesting analogies with the results obtained by Gesner and Kelleher on the Union Carbide polysulfone. Both works indicate the formation of short chain molecules with acid functionalities (sulfonic acid groups) resulting from chain scission reactions.

3.1.18 Silicones

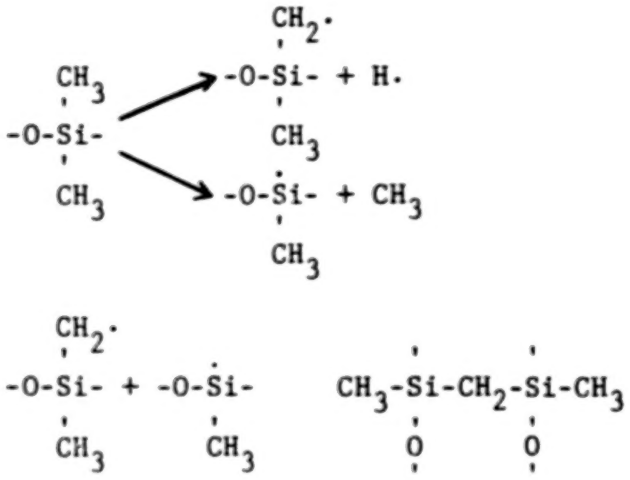
Siegel and Judeikis (ref. 15) studied the photolysis of poly(dimethylsiloxane) samples containing naphthalene as sensitizer. The samples were irradiated in the cavity of an ESR spectrometer. A mercury arc lamp having essentially zero output below 2400Å was employed. The process by which the polymer molecules become excited involves a transfer of electronic energy from naphthalene in an excited triplet level. Decomposition occurs via Si-C and C-H bond rupture. In the initial stage of photolysis, the following reactions take place with essentially equal probability:



All the resulting radicals were identified by means of their ESR spectra, with the exception of the hydrogen atoms that presumably react immediately to form H_2 and $-CH_2\cdot$ radicals.

Zhuzhgov (ref. 17) studied the photolysis of poly(methylphenylsiloxane) in the cavity of an ESR spectrometer. No sensitizer was added, but absorption was promoted by the presence of the phenyl group in the polymer. The ESR spectrum indicated the formation of $CH_3\cdot$ and $-CH_2\cdot$ radicals. Formation of $CH_3\cdot$ radicals appears to involve a two-step process requiring the absorption of two quanta of light (biphotonic mechanism). No evidence was found in the ESR spectrum for the formation of silicon radicals, which must have formed at the same time as the methyl radicals. Volatile products were hydrogen, methane and ethane in the ratio 25:70:5. The same volatile products were also reported by Siegel for poly(dimethylsiloxane) (ref. 13).

Delman (ref. 82) studied the effect of ultraviolet irradiation in air on a methylsiloxane resin. Infrared spectroscopy was employed in this study. Formation of Si-CH_2-Si linkages was observed as a result of irradiation at wavelengths above 2810Å from a Zenon arc lamp:



On the other hand, Si-OH and Si-CH_2-CH_2-Si linkages were formed when the resin was exposed to the shorter wavelength of a mercury vapor lamp. The different effects on the resin induced by the two ultraviolet sources are attributed to the fact that the mercury vapor lamp radiation is sufficiently energetic to cause the excitation of oxygen molecules. The excited oxygen molecules prevented the formation of Si-CH_2-Si linkages by interacting with the Si. radicals (formed by cleavage of Si-C bonds) to produce Si-OH.

Siegel and Stewart (ref. 83) studied the photolysis of poly (dimethylsiloxane) in the vacuum-ultraviolet region (this region starts at 2000Å and extends to shorter wavelengths where it merges with the X-ray region). The wavelengths employed were 1470 and 1236Å. Analysis of the data indicated that the breaking of the Si-CH_3 bond is the most probable reaction occurring at both wavelengths. A comparison with the photolysis of a mixed methyl-

phenyl silicone polymer demonstrated the strong protective effect produced by aromatic substituents in this region of the ultraviolet spectrum. This was determined from quantum yield measurements for the formation of volatile products.

A similar stabilizing effect of aromatic substituents is known to occur when silicones are exposed to high energy, ionizing radiation, presumably because of the ability of the aromatic ring to dissipate some of the absorbed energy before bond rupture occurs (ref. 84).

3.2 Charged Particle Radiation Effects

In this section, various polymer structures are reviewed with a discussion of their behavior when exposed to charged particles or ionizing radiation. Particular attention has been given to studies performed in vacuum and to the effect of particulate radiation (protons, electrons) rather than high-energy electromagnetic radiation (X, gamma). Papers that are specifically related to the effect of a simulated space radiation environment on polyfluorocarbons, silicones and polyimides are discussed separately.

3.2.1 Polyethylene

The irradiation of polyethylene has received the greatest attention because of the beneficial effects of controlled cross-linking by high-energy radiation. The effects of irradiation depend on whether irradiation is conducted in air or under vacuum. Under vacuum, irradiation results in loss of hydrogen and increase in polymer unsaturation. In air, oxidation also occurs with subsequent appearance of carbonyl structures.

Although the principal volatile product of degradation in vacuum is hydrogen, saturated and unsaturated hydrocarbons are also formed, depending upon the degree of branching of the polymer. Harlen and co-workers (Ref. 85) were able to demonstrate that the hydrocarbon products obtained from a branched polymer were dependent upon the nature of the side groups. The similarity between the radiation behavior of polyethylene and low molecular weight alkanes is indicated by the fact that the average G values for hydrogen formation are 4.1 and 4.6 respectively (Ref. 27). (The G value is the number of chemical events which

result from the absorption of 100 electron volts of energy). Chapiro (Ref. 27) demonstrated that below the glass transition temperature (approximately -40°C) $G(H_2)$ is independent of temperature, whereas above -40°C $G(H_2)$ increases with temperature. Exactly the same dependence was demonstrated for cross-linking. This is clearly related to the increased mobility of the hydrogen atoms and polymer radicals above the glass-transition temperature.

Koritskii and co-workers (Ref. 86, 87) have demonstrated the existence in irradiated polyethylene of alkyl radicals which are possible intermediates in the formation of conjugated double bonds:

$$\sim CH_2\text{-}\dot{C}H\text{-}CH{=}CH\sim$$

Charlesby and Pinner (Ref. 86) obtained a value of 0.3 for the ratio of chain-scission to cross-linking in irradiated polyethylene. This indicates that, in spite of the fact that cross-linking predominates in polyethylene, cleavage of carbon-carbon bonds also occurs.

Another effect of irradiation is the formation of unsaturated trans-vinylene structures formed by detachment of an hydrogen molecule from two adjacent carbon atoms:

$$\sim CH_2\text{-}CH_2\sim \longrightarrow \begin{matrix} H & & \sim \\ & C{=}C & \\ \sim & & H \end{matrix} + H_2$$

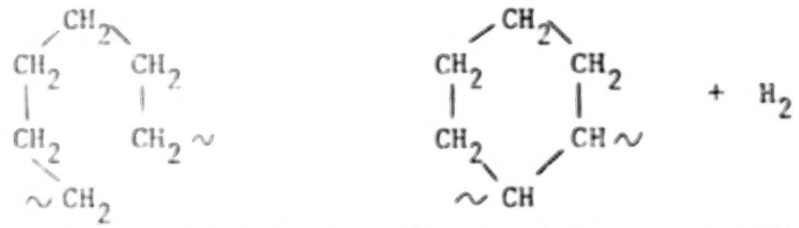
Formation of hydrogen is also involved as a result of cross-linking:

$$2\ \sim CH_2\sim \longrightarrow \begin{matrix} \sim CH\sim \\ | \\ \sim CH\sim \end{matrix} + H_2$$

Since formation of hydrogen is associated with both cross-linking and the development of unsaturation, it is expected that:

$$G(H_2) = G(\text{cross-linking}) + G(\text{trans-vinylene})$$

Charlesby (Ref. 89) found that $G(H_2)$ is slightly larger than expected for this relationship. Chapiro (Ref. 5) suggested that hydrogen may be also produced from intramolecular cyclization, and that this hydrogen accounts for the discrepancy:



In the presence of oxygen, radiation becomes an initiator of oxidation and results in the formation of carbonyl and carboxyl groups. Peroxides are the primary product of radiation-induced oxidation (Ref. 90).

3.2.2 Polypropylene

Both chain scission and cross-linking are found to occur in irradiated polypropylene in approximately equal amounts (Ref. 91, 92). This is not surprising, in view of the fact that polypropylene has a structure intermediate between polyethylene, which predominantly cross-links, and polyisobutylene, which degrades when exposed to radiation.

The most abundant gaseous product is hydrogen, and the second most abundant product is methane (Ref. 93, 94). Traces of higher hydrocarbons with small amounts of CO and CO_2 are also found. Formation of hydrogen is accompanied by formation of unsaturation in the polymer, mainly vinylidene group (Ref. 95).

Many studies have been conducted on the ESR spectra of irradiated polypropylene. The predominant type of radical formed at low temperature (-196°C) is most likely one of the following (Ref. 96, 97, 98, 99):

If the irradiated polymer is allowed to warm to room temperature, or if the irradiation is performed at room temperature, there is a change in the ESR spectrum. These thermally more stable radicals are believed to be allylic radicals having the structures (Ref. 96, 100, 101):

3.2.3 Polyisobutylene

Unlike polyethylene and polypropylene, which cross-link, polyisobutylene degrades when subjected to ionizing radiation (Ref.102,103), as expected from a structure containing a quaternary carbon atom. A study of the effects of various radiation sources indicates that chain scission is a random process that follows first order kinetics (Ref. 104). The degree of unsaturation increases in proportion to the dose, with formation of 1.87 double bonds/scission. Hydrogen and methane are evolved. Isobutylene monomer formation is small but increases with dosage. The amount of monomer produced by radiation is small compared to that produced by pyrolysis (Ref. 104).

3.2.4 Polystyrene

Although polystyrene is rapidly degraded by ultraviolet light, it is one of the most stable polymers towards high energy radiation, owing to the protective action of the benzene ring (Ref. 105). The protective effect of the aromatic ring can be seen by comparing the rate of cross-linking in polystyrene with polyethylene. The G value for cross-linking in polyethylene is 1.0-2.5 but is only 0.035-0.050 in polystyrene (Ref. 106, 107). Cross-linking of polystyrene occurs to the almost total exclusion of chain-scission.

3.2.5 Poly(α-methylstyrene)

Irradiation with 800 keV electrons causes chain-scission of poly(α-methylstyrene) (Ref.103). Unlike polystyrene, chain-scission is the main effect in the irradiation of poly(α-methylstyrene). Once again, it is possible to observe the stabilizing effect of the benzene ring by comparing the G values for chain-

scission of poly(α-methylstyrene) with its aliphatic analog polyisobutylene:

The G value for chain scission in polyisobutylene is 5 (Ref. 108), while the G value for poly(α-methylstyrene) is only 0.25 (Ref. 109).

3.2.6 Unsaturated Polyhydrocarbons

Elastomers derived from dienes and containing high concentration of unsaturated groups have cross-linking and scission rates that are not greatly different from polyethylene. The G value for crosslinking in natural rubber is 1-1.5 and the scission-to-crosslinking ratio is 0.05-0.10 (Ref. 110). It is uncertain whether cross-linking and chain-scission involve consumption of double bonds. Available data on the rate of disappearance of double-bonds during irradiation of unsaturated polymers such as polybutadiene or natural rubber are in wide disagreement (Ref. 111). There is evidence, however, that polybutadiene saturated by addition of methyl mercaptan is more resistant to irradiation than the unsaturated polymer (Ref. 112).

3.2.7 Poly(methylmethacrylate)

The irradiation of poly(methylmethacrylate) (PMMA) has been extensively investigated, and this polymer was found to be readily degraded (Ref. 103,104,113). Alexander and co-workers (Ref. 114) found that degradation is a random chain process and that approximately one ester group was decomposed per each main chain cleavage. Shultz and co-workers (Ref. 115, 116) have

measured changes in molecular weight of 1-mev electron-irradiated PMMA. Since both weight-average and viscosity-average molecular weights are linearly dependent on dosage, it is concluded that no cross-linking occurs during degradation (Ref. 117,118). The most peculiar feature of irradiated poly(methylmethacrylate) is the rapid discoloration, which deepens from yellow to reddish brown with increasing dose. This is surprising, in view of the fact that the same polymer is quite stable to discoloration by ultraviolet irradiation. The color is uniform throughout the bulk of the polymer and is stable in nitrogen or vacuum. In air, the color disappears progressively from the surface throughout the entire sample. Discoloration appears to be due to a transient species, most probably free radicals which are trapped within the solid polymer. The presence of trapped radicals in PMMA was first suggested by ESR determinations (Ref. 119, 120, 121). The presence of these radicals is further attested by the ability of the irradiated polymer to initiate polymerization of monomers (Ref. 122). Wall found that in the solid polymer four months were required for a 100-fold decay in radical concentration at room temperature (Ref. 122). Combrisson and Uebersfeld (Ref.121) observed a decrease in radical concentration only after heating to 80°C. Ohnishi and Nitta (Ref.123) found a long-lived, heat resistant radical of G=0.16, which has an activation energy of decay of 28 kcal/mole. The short-lived radical which is formed by either gamma or electron radiation at 90°K (G=2.5) has been reported to be $-CH_2-C(CH_3)-COOCH_3$ (Ref. 124, 125).

3.2.8 Polyacrylates

Both chain-scission and cross-linking occur when polyacrylates are exposed to high-energy radiation, cross-linking being the predominant effect. Various polyacrylates were studied by Shultz and Bovey (Ref. 126). The value of G(cross-linking) is 0.43-0.57 for all members of the group except the t-butylester, whose value is much lower (0.13-0.16). Chain-scission appears to follow a molecular mechanism that does not involve free radical formation (Ref. 127).

3.2.9 Polyvinylchloride

When polyvinylchloride is irradiated by high energy radiation, a color change takes place which is associated with the formation of a polyene structure formed by dehydrochlorination (Ref. 128, 129, 130).

$$\sim CH_2\text{-}\underset{Cl}{CH}\text{-}CH_2\text{-}\underset{Cl}{CH}\text{-}CH_2\text{-}\underset{Cl}{CH}\sim \longrightarrow \sim CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH\sim + HCl$$

This reaction is similar to the one produced by thermal degradation and by ultraviolet irradiation.

Both cross-linking and chain-scission occur by high-energy irradiation (Ref. 102,103,128,131). An initial decrease in molecular weight and tensile strength is followed by an increase in these properties. At higher doses, insolubilization due to cross-linking takes place. G(cross-linking) is independent of temperature below the glass-transition temperature (80°C), but increases with temperature above the Tg. The deterioration of polyvinylchloride upon exposure to ionizing radiation is greater in air than in vacuum (Ref. 25).

3.2.10 Polyvinylalcohol

Polyvinylalcohol is cross-linked by ionizing radiation in nitrogen whereas chain scission predominates in the presence of air (Ref. 132). The rate of carbonyl group formation upon irradiation depends upon the rate of chain scission. It appears that scission and cross-linking mainly occur at 1,2-glycol groups incorporated in the polymer during polymerization.

3.2.11 Fluorocarbon Polymers

Polytetrafluoroethylene (PTFE) as well as other fluorocarbon polymers undergo chain scission when exposed to ionizing radiation (Ref. 103,133,134). The rapid deterioration of PTFE as a result of irradiation is in striking contrast to its great chemical and thermal stability. Because of the high insolubility of PTFE, the radiation damage has not been studied in terms of molecular weight changes such as osmometry, light scattering or solution viscometry. Other techniques have been used, such as determination of changes in mechanical properties, spectroscopic studies by ESR and NMR, and analysis of gas evolution.

By analogy with polyethylene, which liberates molecular hydrogen in high yield by irradiation, one might expect to find fluorine gas in the irradiation products of PTFE. However, fluorine formation is negligible. Calculations of the energetics of fluorine abstraction and cross-linking in PTFE show that these processes are highly endothermic and unlikely to occur (Ref. 135, 136).

High energy irradiation causes an increase in the crystallinity of PTFE, as demonstrated by measurements of specific volume (Ref.137), density and infrared studies (Ref. 138), and X-ray diffraction measurements (Ref. 139). Pinkerton and Sach (Ref.140) found that the increase in crystallinity is greater in air than in vacuum . The increase in crystallinity is

interpreted on the basis of chain degradation which lowers the molecular weight and increases the ability of the chains to crystallize.

The most noticeable effect of chain scission in PTFE is the loss in mechanical strength. Mechanical strength measurements at various radiation doses were reported by Wall and Florin (Ref.141) and more recently by Hedvig (Ref. 142). Hedvig's data are shown in Table IV and indicate a pronounced deterioration at relatively low radiation doses. Although chain scission is the predominant effect of irradiation, changes in tensile properties in the early stages of irradiation indicate that some cross-linking may also take place (Ref. 141). CF_4 and saturated fluorocarbons up to 6 carbon atoms were identified by analysis of the gases obtained by irradiation under vacuum. In oxygen, CF_2O was also identified (Ref. 143).

All the studies of ESR spectra of irradiated PTFE show a 10-line spectrum attributed to the radical $\sim CF_2\text{-}\dot{C}F\text{-}CF_2\sim$ (Ref. 134 144, 145). This radical combines readily with oxygen (Ref. 145). This combination may be reversed upon heating (Ref. 144).

An important ESR study is that of Hedvig (Ref. 142). Hedvig points out that the in-chain free radicals -CF- in irradiated PTFE are stable up to 150°C and that terminal $-CF_2$ radicals (formed by irradiation under vacuum followed by ultraviolet exposure) are stable up to at least 100°C. Besides the evidence for free radicals, there is some indication of the existence of ionic species in irradiated PTFE, such as a temporary increase in electrical conductivity during irradiation of PTFE (Ref. 24,146,147). Although ions may play some role in fluorocarbon radiation chemistry, the radiation chemistry of this polymer is generally interpreted in terms of free radical

TABLE IV

Mechanical Strength and Elongation at Break of Irradiated PTFE Film*

Treatment	Dose (Mrad)	Mechanical Strength ($kg\ cm^{-2}$)	Elongation at break (%)
Untreated	0	269 ± 15	129 ± 30
Irrad. in vacuo, measured in air	10.4	136 ± 7	10 ± 2
Irrad. in vacuo, oxidized, illuminated with UV light (Hg arc)	10.4	122 ± 5	0.4
Irrad. in air	10.4	0	0

*Film thickness, 0.04 mm. Data of Hedvig (Ref. 142).

mechanisms (Ref. 56).

Polychlorotrifluoroethylene (PCTFE) behaves upon irradiation in a manner quite similar to PTFE (Ref. 131,133,134). Chain scission takes place with no evidence of cross-linking. Very low yields of saturated fluorocarbons are evolved during vacuum irradiation (Ref. 134). The infrared analysis of vacuum irradiated PCTFE shows the presence of double bonds; in air, infrared analysis shows the presence of carbonyl, carboxyl and hydroxyl groups (Ref. 148). ESR studies of PCTFE indicates no detectable radicals in vacuum (Ref. I49).

The copolymer tetrafluoroethylene-hexafluoropropylene degrades by chain scission upon irradiation, in a manner similar to PTFE (Ref. 134). Lovejoy and co-workers (Ref.150) obtained evidence of cross-linking by melt-viscosity measurements. They found that if irradiation is conducted below the glass transition temperature (80°C), the melt viscosity decreases with increasing radiation dose; above the glass transition temperature, the melt viscosity increases with increasing radiation dose.

It is interesting to note that fluorocarbon polymers containing hydrogen, such as polyvinylfluoride, are found to cross-link by irradiation (Ref. 151,152,153). HF evolution has been observed upon vacuum irradiation (Ref. 134).

3.2.12 Polyamides

Aliphatic polyamides such as Nylon 66 become cross-linked with high energy radiation (Ref. 154,155). When aliphatic polyamides are subjected to high-energy irradiation, formation of free radicals occurs as a result of removal of hydrogen from the carbon adjacent to the amide nitrogen (Ref. 156,157,158,159). The most convincing evidence is obtained from ESR spectroscopy of irradiated samples.

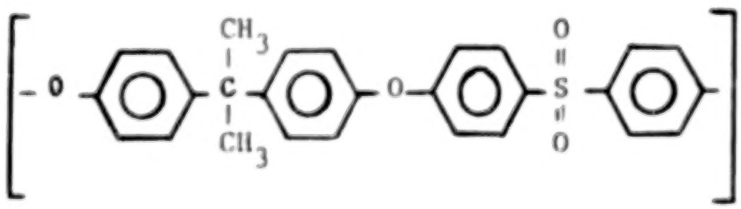
Analysis of the gaseous products of irradiation of polyamides have shown that CO_2, CO, H_2 and CH_4 are formed, with H_2 as the main product. Production of a transient color by irradiation has been associated with the accumulation of free radicals (Ref. 159). The color may be yellow, red or blue depending upon the polyamide structure.

The high degree of specificity in the free radical formation is ascribed to a concentration of energy in the vicinity of the amide group prior to the elimination of the α-proton. Other types of radicals, if they are formed, are expected to disappear in favor of the α-radical by hydrogen transfer reactions. This evidence is supported by experiments on free radical production as a result of mechanically induced degradation.

The rate of free radical decay decreases with increasing the crystallinity of the irradiated polyamide (Ref. 160). As expected, aromatic polyamides are much more stable to high energy irradiation than aliphatic polyamides. The greater stability is demonstrated by comparing the yield of gaseous products obtained by irradiation of the polyamide from m-xylylenediamine and adipic acid (Ref 161) and the polyamide from m-phenylenediamine and isophthalic acid (Ref. 162).

3.2.13 Polysulfones

The radiation stability of the polysulfone derived from bisphenol A and 4,4-dichlorodiphenylsulfone is remarkably high (Ref. 163):



Measurements of gel formation and solution viscosity of irradiated samples indicate that cross-linking and chain scission occur at nearly equal rate. The high radiation stability of the aromatic polysulfones is in great contrast with their poor ultraviolet stability (Ref.164,165), demonstrating once again the protective influence of the benzene ring toward high energy radiation.

Irradiation of the model compound diphenylsulfone results almost exclusively in the elimination of sulfur dioxide and a comparable formation of diphenyl (Ref. 166). Sulfur dioxide is also the main decomposition product of γ-irradiated aromatic polysulfones. RSO_2. radicals have been detected by ESR analysis of irradiated sulfones and polysulfones (Ref. 167).

3.2.14 Polyesters

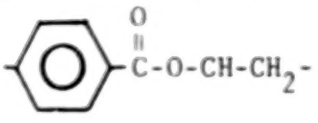
The transmission of polyethyleneterephthalate decreases as a result of irradiation over a wide wavelength range up to 5200Å and discoloration occurs. Partial bleaching is observed on exposure to air, therefore, a distinction has been made between transient and permanent components which are said to make comparable contributions (Ref. 168). It has been suggested that the permanent component is due to polyphenyl groups (Ref. 169). Differences between optical density for samples irradiated and maintained in air (to eliminate the transient component) and unirradiated controls revealed a poorly defined maximum at 3250Å (Ref. 168).

There have been conflicting reports concerning changes in infrared absorption resulting from electron irradiation. In one case a spectrum was presented covering the range 2-15μ in which the only significant change, after a dose of 2000 Mrad was a decrease in absorbance near 2.82μ which was ascribed to a

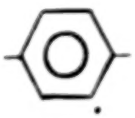
decrease in hydroxyl end-groups (Ref. 170). In other experiments, extensive changes were observed after the same dose and throughout the range 4-15μ, which were attributed to a decrease in crystallinity and formation of polyphenyl systems (Ref. 169). Increased absorption near 3.05μ can be assigned to the formation of carboxyl groups (Ref. 171).

The main gaseous products formed during irradiation are CO_2, CO, H_2 and CH_4 (Ref. 170, 172). The ESR signals of crystalline samples of irradiated polyethyleneterephthalate have been ascribed to the following radicals (Ref. 173).

I (95%)



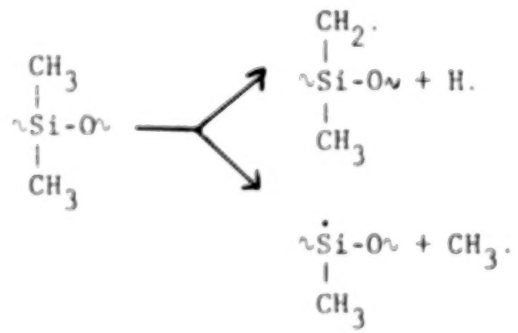
II (5%)



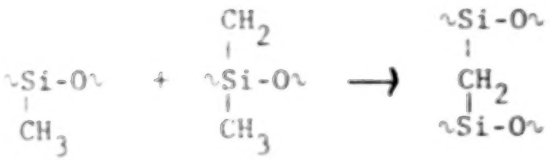
Amorphous samples of PET yield a poorly resolved ESR spectrum. Its features are consistent with radical II but inconsistent with radical I (Ref. 174).

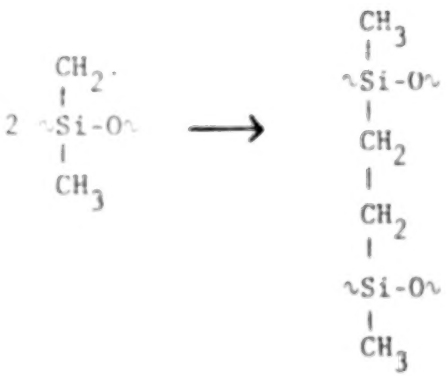
3.2.15 Polysiloxanes

The radiolysis of polydimethylsiloxane causes cleavage of silicon-carbon and carbon-hydrogen bonds:



The radicals formed may react further with formation of three types of cross-links:





Electron irradiation at 25°C produces the cross-linked groups in the ratio 1/2/0.5 respectively for ≡Si-Si≡, ≡Si-CH_2-Si≡, and ≡Si-CH_2-CH_2-Si≡ (Ref. 175). A similar ratio was obtained by irradiation of the model compound $(CH_3)_3Si$-O-$Si(CH_3)_3$, but the yields were lower.

Hydrogen, methane and ethane are formed by the recombination of H· and CH_3· radicals. They are the main gaseous products evolved during irradiation (Ref. 175, 176). Measurements of the effect of radiation intensity and temperature suggest that H· and CH_3· radicals may also abstract hydrogen from the polymer and promote formation of new radical species.

Partial substitution of phenyl groups for methyl groups in the polysiloxane chain increases the radiation stability in terms of both gas evolution and cross-linking. Protection of the radiation sensitive methyl group is increased when phenyl and methyl groups are attached to the same silicon atom (Ref. 177).

A comparison of the radiolysis and photolysis of polydimethylsiloxane (Ref. 178, 179, 180) and polyphenylmethyl siloxane (Ref. 181, 177) clearly indicates that presence of phenyl groups decreases ultraviolet stability whereas radiolytic stability is increased.

3.3 Space Simulation Studies of Charged Particle Effects on Clear Polymers

Silicones, polyimides and fluorocarbon polymers are the materials that have received the greatest attention in space applications. Some recent works dealing with the effects of charged particles radiation on these materials will be reviewed here. These studies are concerned with space applications such as solar cell covers, adhesives, clear (non-pigmented) coatings, and second-surface mirrors.

3.3.1 Fluorocarbon Polymers

Fogdall and co-workers (Ref. 182) reported that metallized FEP Teflon resists reflectance degradation from electron exposure until fluences greater than 10^{15} electrons/cm^2 are reached. All six varieties studied are altered significantly by exposure to 10^{16} 80-keV electrons/cm^2. The Teflon loses its transparent nature and acquires a crazed, mottled gray appearance. This changes the coatings' specular quality to a rather diffuse appearance. Substantial solar absorptance changes result, and reflectance degradation is observed across the entire 0.25- to 2.5-μ wavelength region measured, in all six Teflon coatings studied. Exposure to 20-keV electrons causes less extensive degradation, both in amount and wavelength region affected.

Cunningham and co-workers (Ref. 183) studied the effect of ultraviolet irradiation and charged particle bombardment on bare and metallized FEP Teflon films. The metallized FEP films were: (a) ultraviolet irradiated in vacuum and oxygen; (b) irradiated with 5,10,25 and 30 keV electrons and protoms; and (c) exposed to simultaneous ultraviolet-proton and ultraviolet-electron bombardment. The charged particle irradiations indicate that a measurable change occurs in the spectral reflectance of both silver and aluminum backed material at a dose of about $1x10^{15}$ particles/cm^2, and that this degradation increases as the total dose is increased. This spectral reflectance change appears first and is the most pronounced in the ultraviolet for a given total dose. At a total dose of $1x10^{16}$ particles/cm^2 the surfaces generally look cloudy and oftimes mottled. Upon closer examination this mottling is found to be due to the presence of Litchenberg figures within the teflon-especially in the case of electron irradiation-which are caused by charge storage and subsequent electric discharge. The ultraviolet results confirm that silver coated teflon is stable when irradiated in vacuum and indicate that aluminum coated material undergoes

a small decrease in integrated solar absorptance (i.e., an improvement) when so irradiated. Combined ultraviolet and 20 keV protons tend to retard the damage that occurs with protons alone. However, the 5 keV data do not support such a conclusion.

Schutt (Ref. 184) studied the effect of 30 keV electrons on FEP. Photomicrographs show the presence of Lichtenberg patterns, bubbles and a buckling effect. These effects are discussed in terms of an "electrolysis" mechanisms resulting from charge storage and beam energy thermalization. Expressions are given for surface charge storage and voltage across the sample resulting from such charge accumulation. Buckling is treated on a thermodynamic basis using the Helmholtz free energy and assuming that the distortion develops isothermally. The usefulness of optical measurements for the study of electron damage is questioned. While irradiation with 2-30 keV protons gives reproducible data, irradiation with electrons does not give a degradation sufficiently uniform for optical measurements.

Heaney (Ref. 185) performed optical measurements on aluminum-coated and silver-coated FEP films of various thickness. The data indicate the dependence of solar absorptance and emittance on the Teflon film thickness and the reflectance of the metal underlayer. A correlation between the type of metal used as the reflective coating and the magnitude of radiation - induced degradation shows that Ag-coated Teflon films are less sensitive to damage than aluminized films.

3.3.2 Polyimides

Reflectance degradation in a 2-mil film of Type H Kapton backed by aluminum is strongly dependent upon electron energy. (Ref. 182). The 20-keV electron results are characterized by a peaking of degradation at a wavelength of approximately 0.54μ.

The 50-keV electron results and 80-keV electron results show maximum degradation at a wavelength of approximately 0.60μ. For a fluence of 10^{15} electrons/cm^2, 50-keV degradation is some six times the 20-keV degradation, whereas 80-keV degradation is some eight times that at 20-keV.

3.3.3 Silicones

Pellicori studied the optical properties (Ref. 186) and the radiation stability (Ref. 187) of various silicone bonding agents. Fused silica discs bonded with 0.06-mm layers of various silicone elastomers were subjected to dosages between 1 and $2x10^6$ rad of 10 MeV electrons. The transmittance of the samples was determined before and after exposure. The best material in terms of radiation stability, low outgassing and thermal shock resistance was DC93-500.

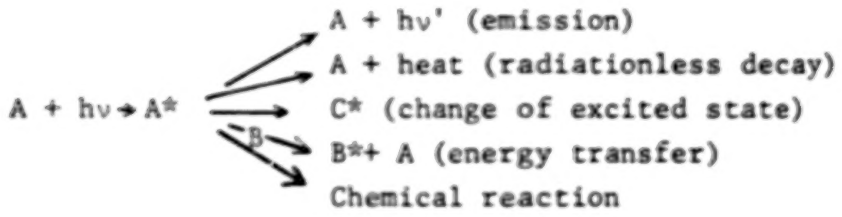
The effects of charged particle irradiation on various silicone encapsulating polymers has been investigated (Ref. 188). Results of irradiation with 2.7 MeV electrons for fluences of $3x10^{16}$ electrons/cm^2 show that the most stable of the polymers tested are Sylgard 182 and RTV-615.

The outgassing behavior of silicones in a high-vacuum environment and the characterization of volatile products by liquid-gas chromatography has been reported (Ref. 189, 190).

4. RATIONALE FOR MATERIAL SELECTION

4.1 General Approach

The various modes by which a polymer dissipates absorbed ultraviolet energy are the following:



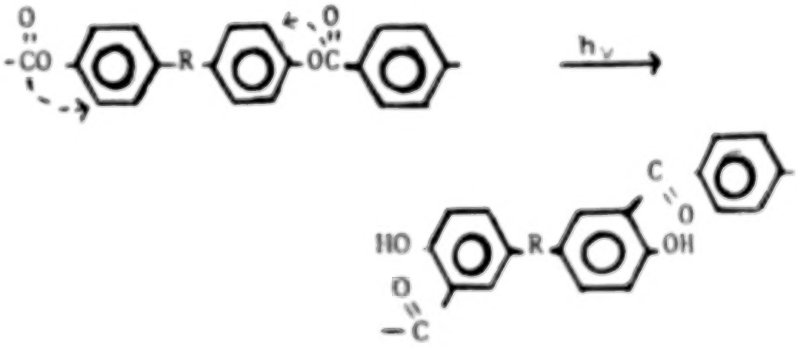
Polymer stability to ultraviolet radiation requires one of the following conditions: (a) ultraviolet transparent structure; (b) structure capable of completely dissipating absorbed ultraviolet energy by non-chemical methods; (c) structure capable of completely dissipating absorbed ultraviolet energy by a chemical rearrangement that does not involve chain cleavage or other undesirable degradative effect.

In the design of an experimental program aimed at the development of materials with improved stability to the ultraviolet radiation environment of space, we have given special consideration to the following basic approaches: (1) preventing energetically favored photodegradation mechanisms (e.g., Norrish Type II) by appropriate polymer structural modifications; and (2) utilizing mechanisms by which ultraviolet absorbed energy is effectively dissipated, namely, fluorescence, radiationless decay, energy transfer to acceptor molecules, and photorearrang-

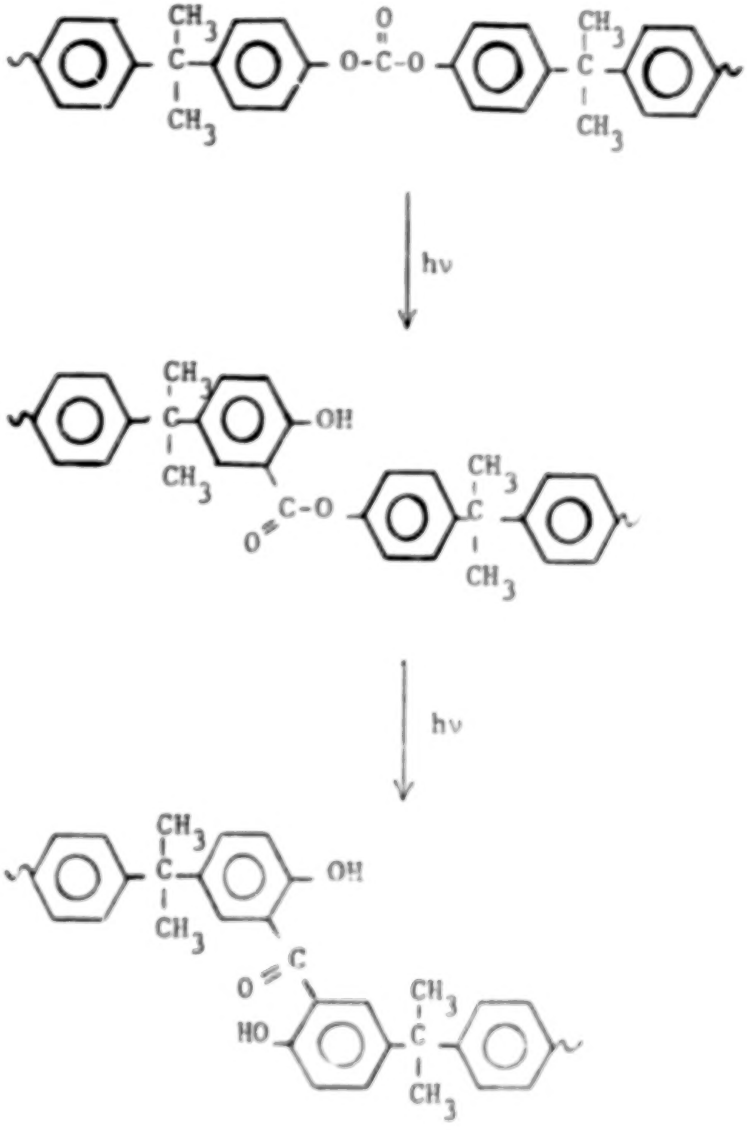
ments not involving homolytic cleavage. Therefore, we have studied the feasibility of these approaches and we have initiated an experimental program aimed at verifying the applicability of these concepts to the development of ultraviolet-stable polymer structures. The approaches considered and the rationale for selection of polymer structures for ultraviolet testing are described in the following paragraphs.

4.2 Photorearrangements of Polymer Structures

An unconventional approach to the problem of ultraviolet stabilization involves the use of structures capable of dissipating absorbed ultraviolet energy by a photo-induced rearrangement. The chemical rearrangement produced should not be accompanied by cleavage reactions and should not have appreciable effect on the physical and optical properties of the polymer. Along this line of thought, we have reviewed the available literature on the photo-Fries reaction to determine whether this type of rearrangement can be effectively utilized to dissipate absorbed ultraviolet energy in polymer structures. The photo-Fries rearrangement of aromatic polyesters and polycarbonates does not produce chain cleavage. Furthermore, it leads to the formation of a o-hydroxybenzophenone structure that may further stabilize the polymer against photolytic degradation. The Fries rearrangement of aromatic polyesters has been described by Maerov (Ref. 191), Rode and co-workers (Ref. 192), Cohen and co-workers (Ref. 193):

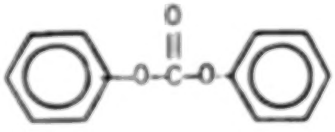


The Fries rearrangement of aromatic polycarbonates has been described by Bellus and co-workers (Ref. 194) and Mullen and co-workers (Ref. 195). It involves a stepwise rearrangement to dihydroxybenzophenone via a phenylsalicylate structure:

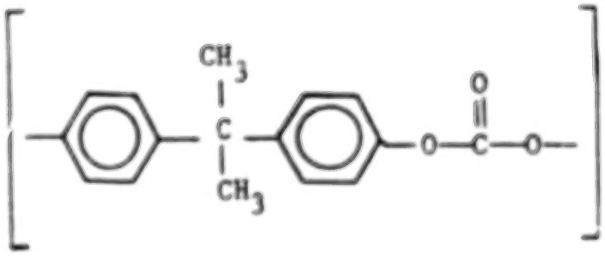


The rearrangement follows essentially the same mechanisms as the photo-Fries of simple organic molecules, such as the rearrangement of phenylacetate into o- and p-hydroxy benzophenone (Ref. 196). In the case of the polyesters and polycarbonates previously mentioned, the para position is occupied and the rearrangement takes place exclusively in ortho.

We investigated the photolysis of aromatic carbonate structures capable of undergoing ultraviolet induced Fries rearrangements. We utilized ESR techniques and in-vacuo reflectance spectroscopy for the study of the photolysis of high purity diphenylcarbonate (I) (a model compound) and bisphenol-A polycarbonate (II):



(I)



(II)

4.3 De-excitation of Absorbed Energy

This approach involves the development of a polymer structure capable of dissipating absorbed ultraviolet energy without producing a chemical change. The general modes by which a photoexcited molecule may return to the ground state were discussed in section 4.1 of this report. Ultraviolet stabilization may result from three general mechanisms of energy dissipation: (1) quenching of the polymer excited state by energy transfer to acceptor molecules; (2) de-excitation by radiationless decay (emission of heat); (3) de-excitation by fluorescence or phosphorescence. These mechanisms will be reviewed in the following paragraphs.

4.3.1 Triplet Quenching by Energy Transfer

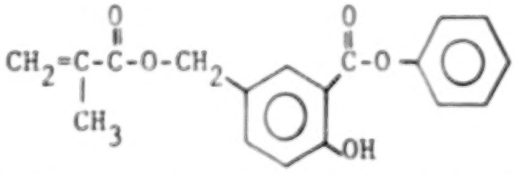
A typical example of this approach is the use of naphthalene (either as additive or copolymerized vinylnaphthalene) for quenching the excited triplet state of aromatic vinyl polymers, such as polystyrene (Ref. 197, 198, 199), polyvinylketone (Ref. 200, 201), or polyvinylbenzophenone (Ref. 202). However, this approach is limited to excited polymer molecules in the triplet-state, such as aromatic vinyl polymers, and does not have a general applicability.

4.3.2 Radiationless Decay

This approach involves the use of a polymer structure capable of reverting from the photo-excited state to the ground state by radiationless transitions. Since this is the mechanism of action of conventional ultraviolet stabilizers, the same concepts that are applicable to the design of ultraviolet stabilizer additives are also applicable to the design of a poly-

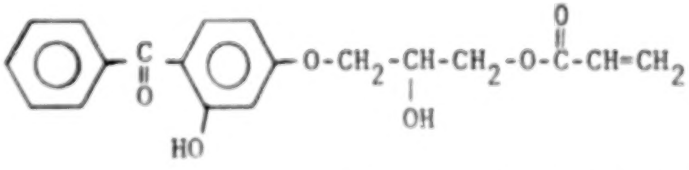
meric material possessing the structural characteristics of a ultraviolet stabilizer incorporated into the polymer molecule.

We found several examples in the literature concerning the use of reactive ultraviolet stabilizers. Unlike conventional ultraviolet stabilizers, these are reactive vinyl and acrylic compounds capable of copolymerizing with conventional monomers to form ultraviolet stable copolymers. These compounds are generally characterized by the presence of an o-hydroxy group capable of forming an intramolecular six-membered hydrogen-bonded ring capable of deactivating the excited state through a radiationless transition so that the energy is given up in the form of harmless heat. It has been reported that these reactive ultraviolet stabilizers overcome the many problems of conventional ultraviolet stabilizers (e.g., volatility, extractability, migration, incompatibility, decomposition during processing). Fertig (Ref. 203) reported the use of salicylates as comonomers:



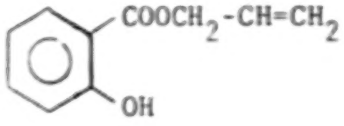
Copolymers of 2% of this material with vinylacetate or vinylchloride provide effective ultraviolet stabilization.

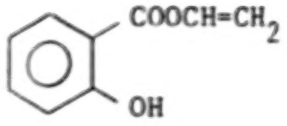
Another example is the use of monomers containing hydroxybenzophenone (Ref. 204):



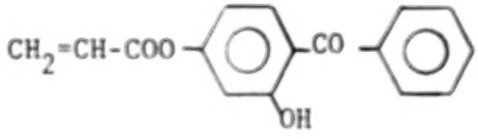
This compound was (a) homopolymerized and blended with PVC, polyvinylacetate, polyvinylidene chloride, polystyrene, polymethyl methacrylate; (b) copolymerized with the same monomers. Effective ultraviolet stabilization was observed.

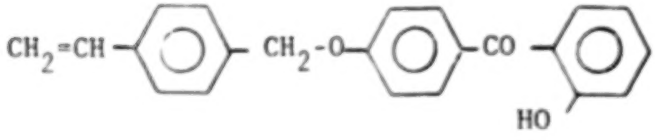
Other examples of ultraviolet absorbing salicylate comonomers are found in the patent literature (Ref. 205):

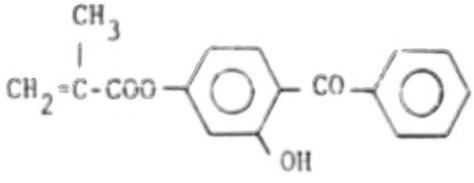




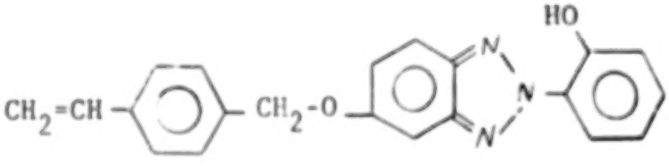
There are more examples in the patent literature of ultraviolet absorbing o-hydroxybenzophenone comonomers (Ref. 206, 207, 208, 209):



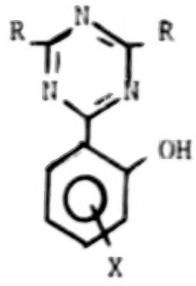




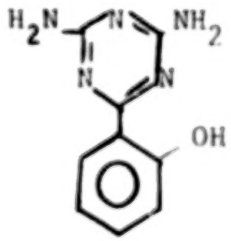
Comonomers containing o-hydroxyphenylbenzotriazole have also been reported (Ref. 210, 211):



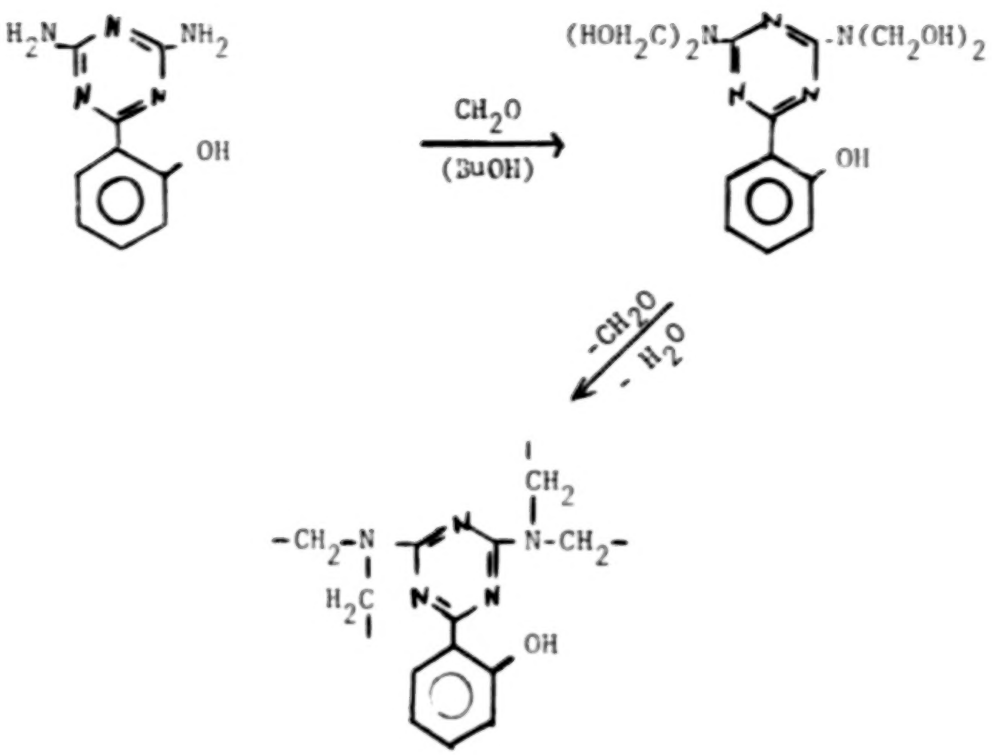
A number of patents cover the use of o-hydroxyphenyl triazine derivatives as ultraviolet stabilizers (Ref. 212):



Surprisingly, there is no reference in the literature to the use of monomeric compounds containing the o-hydroxyphenyltriazine structure for the synthesis of ultraviolet stable polymers. Therefore, we decided to investigate the feasibility of using o-hydroxybenzoguanamine (o-hydroxyphenyldiaminotriazine) as a reactive intermediate:



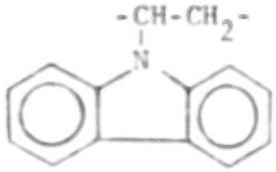
This intermediate is particularly interesting because of its similarily with benzoguanamine, that forms aminoplastic resins by reaction with formaldehyde. Thus, we synthesized o-hydroxybenzoguanamine that was subsequently utilized as a monomer for the synthesis of partially butylated amino resins by reaction with paraformaldehyde in n-butanol:

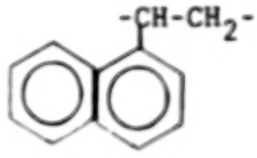


Unlike the other polymer structures containing ultraviolet-stabilizing groups that have been reported in the literature, this polymer structure does not possess ultraviolet-absorbing groups other than the ultraviolet-stabilizing o-hydroxyphenyl-triazine unit. The homopolymer of formaldehyde with o-hydroxy-benzoguanamine was synthesized as well as copolymers containing mixtures of benzoguanamine and o-hydroxybenzoguanamine at various ratios. The homopolymer of benzoguanamine with formaldehyde was also synthesized.

4.3.3 Fluorescence

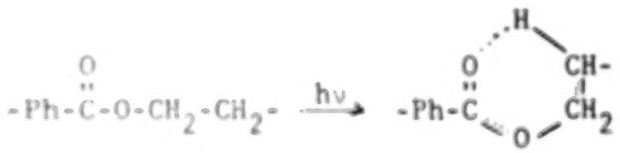
Another mechanism of energy dissipation involves reversion to the ground state by photon emission: the excited molecule re-radiates part of the energy at a longer wavelength as fluorescence or phosphorescence, depending on whether the excited state is a singlet or a triplet. Fluorescence emission properties of poly-N-vinylcarbazole and polyvinylnaphthalene have been reported by Johnson and co-workers (Ref. 213) and by David and co-workers (Ref. 214, 215). Because of their fluorescence characteristics and their ability to form clear films, poly-N-vinylcarbazole and polyvinylnaphthalene were selected for ultraviolet exposure testing:





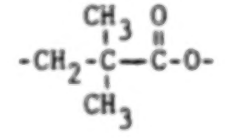
4.4 Prevention of Norrish Type II in Aliphatic Polyesters and Polycarbonates

Photolysis of polyesters involves decomposition of the ester groups by a Norrish Type II process. It involves a molecular mechanism with formation of an intermediate 6-atom transition stage. For example, in the case of polyethylene-terephthalate, this decomposition reaction can be represented as follows:



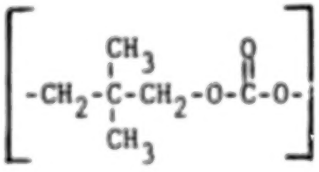
$$\text{-Ph-COOH} + \text{CH}_2\text{=CH-}$$

It was thought that a polyester structure with no hydrogen on the carbon atom in β position should possess improved ultraviolet stability since the energetically favored Norrish Type II could not take place. Therefore, we decided to investigate polyester and polycarbonate structures characterized by (a) completely aliphatic structure to reduce ultraviolet absorption and (b) structure disubstituted on the β-carbon to prevent Norrish Type II photodegradation. A polyester structure that meet these requirements is polypivalolactone, (I), that was selected for ultraviolet testing:

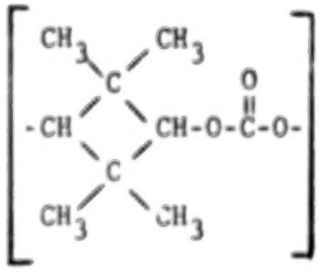


(I)

Two polycarbonate structures meeting the same requirements were also investigated. They are the polycarbonates from neopentylglycol (II) and from tetramethylcyclobutanediol (III):



(II)

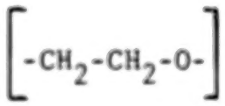


(III)

4.5 Ultraviolet Transparent, Aliphatic Polyethers

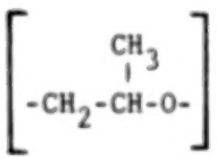
Since there can be no ultraviolet damage without absorption, the development of a polymer structure highly transparent down to 2000A appears to be an interesting approach to the problem of ultraviolet stability.

A typical example of transparent structure are the methylsilicones. Unfortunately, methylsilicones are quite sensitive to the presence of impurities that cause absorption and initiate photodegradation (Ref. 216). We examined other polymer structures that are fundamentally transparent to the short wavelength ultraviolet and we selected two samples of poly(ethylene oxide) (MW 20,000 and 5,000,000) for ultraviolet exposure testing:

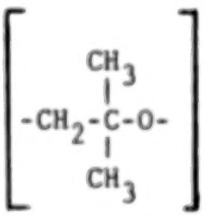


(I)

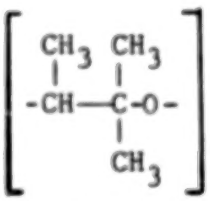
In addition, other substituted alkylene oxides were also investigated. These include poly(propylene oxide) (II), poly(dimethylethylene oxide) (III), poly(trimethylethylene oxide) (IV), poly(tetramethylethylene oxide) (V), and poly(cyclohexene oxide) (VI):



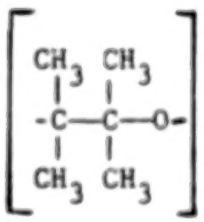
(II)



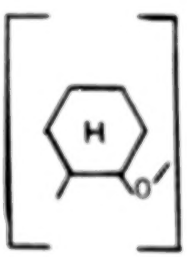
(III)



(IV)



(V)



(VI)

5. ULTRAVIOLET EXPOSURE TESTS

The basic criterion employed for determining the damage produced by irradiation in a simulated space environment was the change in the optical properties of the material. The materials selected for ultraviolet exposure testing were coated on polished aluminum substrates and irradiated in vacuum at one solar constant. "In-situ" reflectance measurements were taken at various times. In some cases, a final measurement was taken after bleaching with oxygen. The experimental procedures employed and the conditions of the tests are described in section 6.3. The reflectance data at various radiation doses are presented in the Appendix both in graphical and tabular form. The graphs show the reflectance curves (initial and final measurements) over the whole region 0.25-2.6μ. The tables show the solar absorptance (α_s) of the samples at various exposure times. As a general rule, optical damage manifests itself as a progressive decrease in ultraviolet transmittance (measured as double reflectance) that may reach the visible range and give rise to yellowing of the polymer. Therefore, the observation of changes occurring in this region of the spectrum is very critical. In some cases, a "bleaching" effect was produced, resulting in a slight increase in reflectance.

5.1 Results of Preliminary IITRI Tests

The results of these preliminary, short-term tests, have been utilized in subsequent work as a basis for a more detailed experimental program. The main conclusions of these tests will be briefly summarized here. Detailed results of these tests were presented in a previous report (Ref. 2).

With the objective of determining whether the Fries photorearrangement is a feasible technique of polymer stabilization, a study of the photolysis of diphenylcarbonate (a model compound) and bisphenol-A polycarbonate was performed by

using ESR techniques and in-situ reflectance measurements. These studies indicated that, in conjunction with the photo-Fries, other secondary degradative processes occur that lead to cleavage or discoloration. It was concluded that the Fries rearrangement is not a feasible approach to the problem of ultraviolet stabilization, and no further work was performed on these polymers.

The utilization of an aliphatic polyester in which the Norrish type II photodegradation reaction is prevented by disubstitution on the carbon atom in β-position with respect to the in-chain oxygen link was also investigated. Poly-pivalolactone was utilized as a model polymer. Irradiation up to 200 hr caused little change in reflectance, suggesting that this approach should be further explored.

Polyvinylcarbazole exhibited unusually high stability up to 200 hr, and a decision was made to expand this study to include, in addition to polyvinylcarbazole, other polymers exhibiting fluorescence emission.

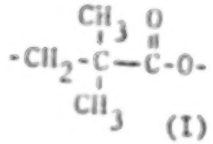
Preliminary tests on amino resins containing o-hydroxy-benzoguanamine as ultraviolet stabilizer/comonomer showed an increase in ultraviolet stability with increasing o-hydroxy-benzoguanamine content. This approach was explored in greater detail in subsequent work.

Two samples of poly(ethyleneoxide) of different molecular weight (M.W.=20,000 and 5,000,000) were tested and found to possess excellent stability. In particular, the poly(ethylene-oxide) with a molecular weight of 5,000,000 showed no reflectance degradation; on the contrary, a definite improvement in reflectance in the far ultraviolet was observed. Because of these promising results, this study was subsequently expanded to include aliphatic polyethers from substituted 1,2-epoxides.

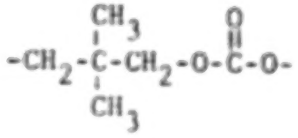
5.2 Results of Ultraviolet Exposure Tests Performed at the Langley Research Center

The experimental procedures employed and the conditions of the test are described in Section 6.3. The materials tested can be divided in the following groups:

(a) Aliphatic polyesters and polycarbonates in which the energetically favored Norrish type II photodegradation reaction is prevented by disubstitution on the carbon atom in β-position with respect to the in-chain oxygen atom. The materials tested included polypivalolactone (I) and the polycarbonate of neopentylglycol (II):

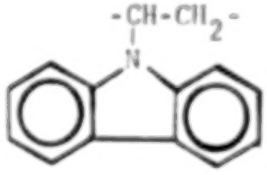


(I)

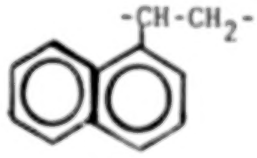


(II)

(b) Polymers exhibiting fluorescence emission. The materials tested in this group included polyvinylcarbazole (III) and polyvinylnaphthalene (IV)

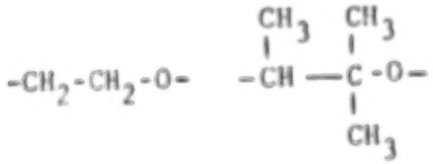


(III)

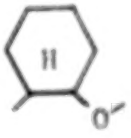


(IV)

(c) Ultraviolet transparent aliphatic polyethers. Materials tested in this group included poly(ethyleneoxide) (V), poly(trimethylethyleneoxide) (VI), and poly(cyclohexeneoxide) (VII):



(V) (VI)



(VII)

(d) Thermosetting partially butylated amino resins containing o-hydroxybenzoguanamine as a UV stabilizer/comonomer. These resins were synthesized by condensation of o-hydroxybenzoguanamine/benzoguanamine/formaldehyde in n-butanol. The homopolymer formaldehyde/o-hydroxybenzoguanamine was tested as well as copolymers containing mixtures of benzoguanamine and o-hydroxybenzoguanamine. The homopolymer of benzoguanamine with formaldehyde was also tested for reference purpose.

Polypivalolactone (I) was tested for 800 ESH. It exhibited a pronounced decrease in reflectance both in the UV and visible region (Fig. A-1). Similar behavior was exhibited by the polycarbonate of neopentylglycol (II), that was tested up to 1481 hours of irradiation (Fig. A-2, Table A-2).

Two samples of polyvinylcarbazole (II) were tested, the first sample for 1481 ESH (Fig. A-3, Table A3) the second sample for 1895 ESH (Fig. A-4, Table A-4). Solar absorptance measurements indicate initial good stability followed by an increase in the rate of degradation at long exposure times. This was particularly evident with the second sample, which showed a $\Delta\alpha_s$ of only 0.012 after 1040 ESH. Subsequent degradation took place at a much faster rate, resulting in a $\Delta\alpha_s$ of 0.051 after 1894 ESH.

Polyvinylnaphthalene (IV) was tested for 1485 ESH (Fig. A-5, Table A-5). It exhibited some UV and visible damage during the first 1100 hours of irradiation but essentially no damage for subsequent doses. The solar absorptance of this material was unusually low for an aromatic polymer (α_s = 0.194 at 0 ESH).

Two samples of poly(ethyleneoxide) having a molecular weight of 5,000,000 were irradiated in separate tests for a total exposure time of 1481 ESH (Fig. A-6, Table A-6) and 1946 ESH (Fig. A-7, Table A-7). The results of these experiments confirmed the excellent stability of this material. Irradiation causes an improvement in transparency as indicated by values of α_s that decrease with increasing exposure time. Values of α_s dropped from 0.181 (0 ESH) to 0.156 (1481 ESH) in the first sample and from 0.180 (0 ESH) to 0.138 (1946 ESH) in the second sample. This improvement was partially lost as a result of air bleaching at the end of the test.

Poly(trimethylethyleneoxide) was tested for 611 ESH (Fig. A-8, Table A-8). It exhibited some reflectance degradation in the UV and visible region partially compensated by a reflectance increase in the IR region. The overall effect on α_s was an increase from 0.260 to 0.280.

Poly(cyclohexeneoxide) was tested twice. The first sample was exposed for 890 ESH (Fig. A-9, Table A-9), the second sample for 464 ESH (Fig. A-10, Table A-10). Pronounced reflectance degradation was observed on both samples. Later it was found by elemental analysis that the carbon content of the polymer was 1% higher than the calculated value, suggesting that presence of impurities may be responsible for the observed instability.

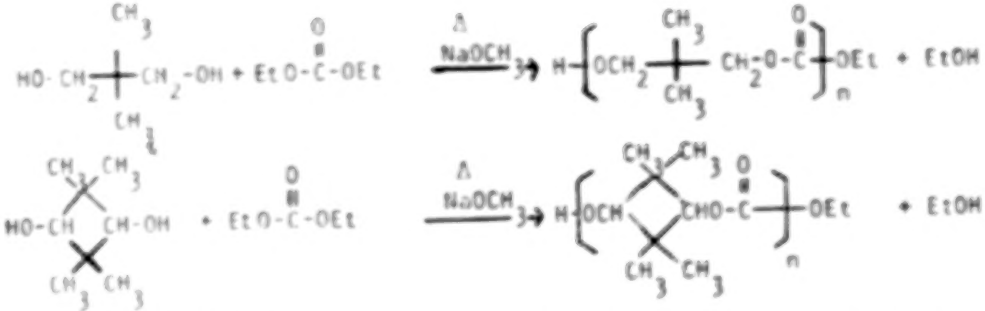
The polymer of benzoguanamine-formaldehyde was tested for 611 ESH (Fig. A-11, Table A-11). Reflectance degradation took place in the UV-visible region, while an improvement in reflectance was observed in the IR region. The copolymer of benzoguanamine/formaldehyde with 2% o-hydroxybenzoguanamine was tested for 484 ESH (Fig. A-12, Table A-12). The inital value of α_s was quite low (α_s=0.196 at 0 ESH), but UV irradiation caused reflectance degradation over the whole region of the spectrum. Air bleaching at the end of the test caused a further drop in reflectance. The copolymer of benzoguanamine/o-hydroxybenzoguanamine/formaldehyde (molar ratio benzoguanamine/o-hydroxybenzoguanamine = 50/50) exhibited degradation in the UV-visible region and an improvement in the IR region (Fig. A-13, Table A-13). A similar effect was observed with the homopolymer o-hydroxybenzoguanamine/formaldehyde (Fig. A-14, Table A-14), that was tested for 936 ESH. Ultraviolet damage was less pronounced, and no change in reflectance was observed during the last 200 hours of irradiation. IR analysis of the polymer (Fig. 11) revealed traces of carbonyl groups that may have been formed as a result of oxidation during polymerization and curing.

6. EXPERIMENTAL

6.1 Polymer Synthesis

6.1.1 Polycarbonates

Synthesis of neopentylglycol polycarbonate and tetramethyl cyclobutanediol polycarbonate was attempted by ester interchange with diethylcarbonate catalyzed by sodium methoxide:



The procedure employed was essentially identical to the one reported by Surel and Pohoryl (Ref. 217).

To a mixture of neopentylglycol, 20.75g (0.199 mole), and diethylcarbonate, 24.11g (0.204 mole), was added sodium methoxide powder, 0.055g (0.001 mole), in a 50 ml flask fitted with a condenser. The flask equipped with a stirrer was placed in an oil bath and the temperature was slowly brought to 117-119°C when the ethanol began to distil. After 2.5 hours, 11 ml distillate was collected at 77 to 80°C. An additional 1.8 ml was distilled at aspirator pressure making the total 12.8 ml (theoretical, 14.8 ml). The viscous residue was crystallized with benzene-petroleum ether (30 - 60) affording 19.34g (74.4%) of white powder.

In a similar manner, a mixture of tetramethylcyclobutanediol, 15.06g (0.104 mole), and diethylcarbonate, 12.53g (0.11 mole), catalyzed by sodium methoxide, 0.105g (0.0019 mole) was reacted in an oil bath at 117 to 119°C. In 1 hour, 8 ml (theoretical, 7.6 ml) ethanol was collected at 79 -80°C. After no further distillate was obtained by evacuation with the mechanical pump, the viscous residue was treated with benzene and petroleum ether (30 - 60). After separation of some crystalline material, a viscous filtrate

6.1.1.1. Preparation of Neopentylglycol-bis- (ethylcarbonate)

Neopentylglycol (30.3g, 0.29 mole) was reacted with an excess of diethylcarbonate (176 ml, 1.46 mole) in the presence of sodium methoxide catalyst (0.26g, 0.0045 mole). The mixture was heated at 125°C with stirring. After 1 hr, ethanol started to distill. Approximately 40 ml of distillate were collected over a period of 1 3/4 hr. The resulting reaction mixture was diluted with benzene and washed until neutral with 2% HCl in water. The organic phase was separated, dried and distilled. The concentrated residue was fractionally distilled to give a total of 43.1g (60% yield) of clear liquid, b.p. 102-103°C/0.6mm Hg. The infrared spectrum of this material is shown in Figure 1.

Analysis: calculated for $C_{11}H_{20}O_6$: C=53.21; H=8.12. Found: C=53.30; H=8.40.

6.1.1.2. Polymerization of Neopentylglycol-bis-(ethylcarbonate)

The catalyst employed for polymerization was a butanol solution of sodium hydrogen tetrabutoxytitanate. This was prepared by adding sodium (0.53g, 0.023 mole) to a mixture of dry butanol (50 ml) and tetra-n-butyltitanate (7.4g, 0.022 mole). Additional butanol was added to reach a total volume of 100 ml.

Neopentylglycol-bis-(ethylcarbonate) was placed in a flask fitted with a condenser and a nitrogen inlet tube reaching the bottom of the flask. The catalyst (0.05 ml) was measured with a micropipet and added. The flask was heated in an oil bath at 220-230°C. Polymerization was accompanied by distillation of diethylcarbonate. The amount of diethylcarbonate collected was 1.7 ml (theor. 2.0 ml).

Vacuum was applied with an aspirator to complete polymerization and removal of diethylcarbonate. The resulting viscous yellow oil was dissolved in methylene chloride, the solution was filtered and coagulated in methanol to give 0.337g of white, powdery polymer (yield, 66%) The melting point of the product was 105-108°C and the inherent viscosity was 0.34 (25°C, 0.5%) in dichloroethane. The infrared spectrum of this polymer is shown in figure 2.

6.1.1.3. Preparation of Tetramethylcyclobutanediol-bis-(ethylcarbonate)

Tetramethylcyclobutanediol (25.2g, 0.17 mole) was reacted with diethylcarbonate (110 ml, 0.91 mole) in the presence of sodium methoxide (0.33g, 0.006 mole). Distillation of ethanol took place while the reaction mixture was heated at 130-140°C. The reaction product was diluted with benzene and washed with 2% HCl in water. The organic phase was dried and concentrated. The residue was vacuum distilled to yield 31.3g (63.9%) clear liquid, b.p. 115-116/10mm Hg.

Analysis: calculated for $C_{14}H_{24}O_6$: C=58.32; H=8.39.
Found: C=58.33; H=8.64.

6.1.1.4. Polymerization of Tetramethylcyclobutanediol-bis-(ethylcarbonate)

The apparatus and technique used were essentially the same as described for the neopentylglycol polycarbonate. Tetramethylcyclobutanediol-bis-(ethylcarbonate) (3.0g, 0.01 mole) was polymerized in the presence of a catalytic amount of sodium hydrogen tetrabutoxytitanate (0.03 ml). The mixture was heated at 254°C and the temperature gradually increased to 273°C while diethylcarbonate was distilled. The residue was evacuated to 0.7mm Hg at a temperature of 240°C. The white solid residue (1.35g) was dissolved in methylene chloride, the solution was filtered and coagulated in methanol to

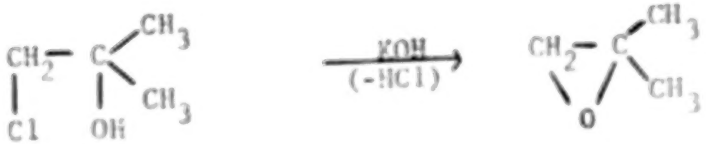
yield 1.14g (yield 61%) of white powdery polymer of low molecular weight having a melting point of 234-242°C and an inherent viscosity of 0.21 in dichloroethane (0.5%, 25°C). The infrared spectrum of this polymer is shown in Figure 3.

6.1.2 Polyethers

Various substituted poly(alkylene oxides) have been synthesized by ring opening of epoxide monomers by using cationic and/or organometallic initiators. The intermediate epoxides were synthesized from the chlorohydrins (by dehydrochlorination) or from the olefins (by oxidation with peracetic acid).

6.1.2.1 Preparation of 1,1-Dimethylethylene Oxide

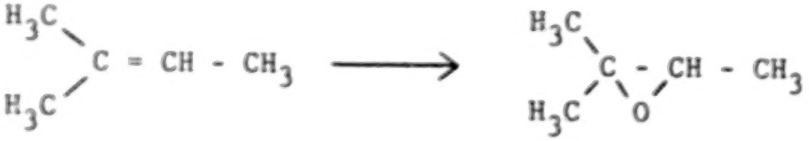
1,1-dimethylethylene oxide (isobutylene oxide) was prepared by dehydrohalogenation of 1-chloro-2-methyl-2-propanol(Ref 218):



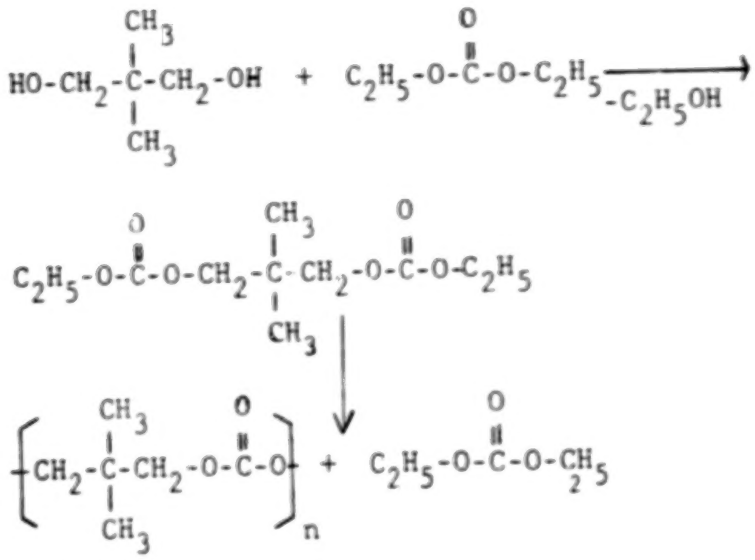
1-chloro-2-methyl-2-propanol (72g) was slowly added to potassium hydroxide (200g) in a 500 ml flask equipped for distillation. An exothermic reaction occurred with formation of the epoxide that was fractionally distilled. The heat of reaction was sufficient to promote distillation of the epoxide. The rate of chlorohydrin addition was adjusted as required to control the rate of distillation. After the addition was completed, heat was applied to the flask to complete the distillation of the epoxide. The 1,1-dimethylethylene oxide was isolated as a clear liquid, b.p. 49.5-51°C (reported 50.2-50.5°C). Yield, 36g (75%).

6.1.2.2. Preparation of Trimethylethylene Oxide

The synthesis of this epoxide was performed by oxidation of trimethylethylene with peracetic acid:



A 3-necked flask equipped with a thermometer, mechanical stirrer and dropping funnel was employed. Sodium carbonate (85g), methylene chloride (100 ml) and trimethylethylene (50g) was added. The flask was placed in an ice bath and cooled while stirring. To this stirred mixture, 40% peracetic acid (122g, 106 ml) was added at such a rate as to keep the temperature below 15°C. The addition was completed in two hours. The mixture was stirred for 1 hr at ice bath temperature, removed from the ice bath and allowed to stir another hour at room temperature. Water (150 ml) was added and the organic phase was extracted with two 100 ml portions of methylene chloride. The organic phase was repeatedly washed with ferrous sulfate solution in order to decompose unreacted peroxide. When the red color disappeared (negative peroxide test), the methylene chloride solution was dried over sodium sulfate for 48 hours. Fractional distillation yielded 18.7g (31%) of clear liquid, b.p. 70-72.5°C (lit. 72-73°C) was recovered. This procedure resulted in the formation of low molecular weight materials. In order to obtain higher polymers, a two-step procedure was employed involving (1) the preparation of the bis-ethylcarbonate of the diol, and (2) the polymerization of this intermediate via carbonate interchange reaction. In the case of neopentylglycol, the reaction scheme is the following:

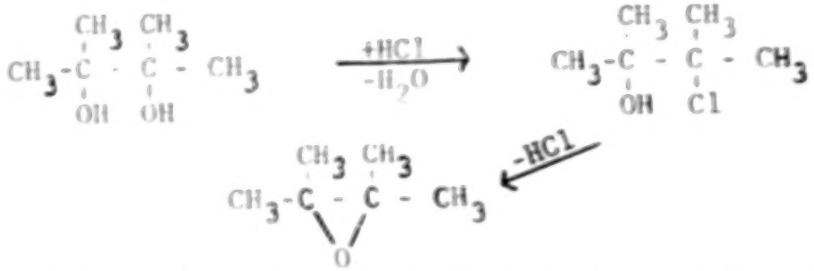


The bis-ethylcarbonate of neopentylglycol and tetramethylcyclobutanediol could be synthesized in good yields. The composition of these intermediates was confirmed by elemental analysis. Polymerization of neopentylglycol-bis-(ethylcarbonate) led to the formation of a polycarbonate with an inherent viscosity of 0.34 in dichloroethane (0.5%, 25°C). This material exhibited good film-forming characteristics by solution casting. The polycarbonate of tetramethylcyclobutanediol had an inherent viscosity of only 0.21 and was not a film-forming material.

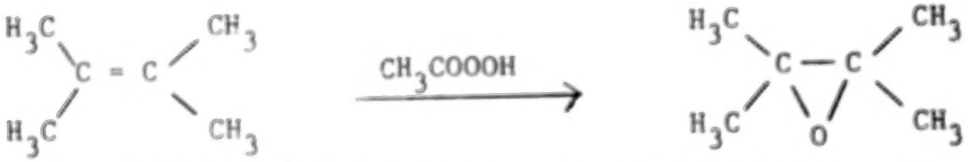
6.1.2.3 Preparation of tetramethylethylene oxide

An approach similar to the one employed for the synthesis of dimethylethylene oxide was utilized for the synthesis of tetramethylethylene oxide. The intermediate chlorohydrin (3-chloro-2,3-dimethyl-2-butanol) was synthesized by reaction of anhydrous pinacol with a

stoichiometric amount of hydrogen chloride gas:



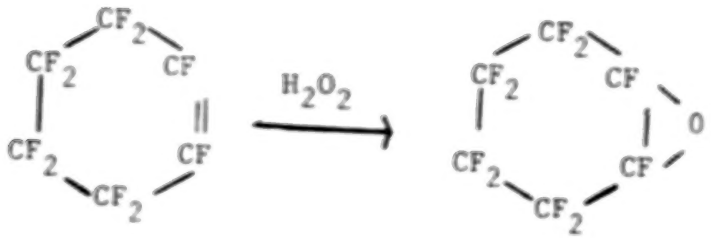
Pinacol (104g) was melted by heating at 50°C. Dry hydrogen chloride gas diluted with nitrogen was bubbled in the liquid pinacol over a period of 2 hours. The color of the solution turned progressively darker during addition. After the addition was completed (37g), the solution was precipitated by an equal volume of water and the product filtered and washed with water. The chlorohydrin obtained was dried in an oven under vacuum at 30-40°C. Because of difficulties in the purification of this material, this method of synthesis was abandoned and another approach was employed involving the direct oxidation of 2,3-dimethyl-2-butene (tetramethylethylene):



The same procedure and equipment utilized for the synthesis of trimethylethylene oxide was employed. Fractional distillation of the reaction product through a Vigreaux xolumn yielded 26.3g of tetramethylethylene oxide, b.p. 90-91.5°C (lit. 90-91°C). Redistillation of lower boiling fractions yielded additional 20.3g of product, b.p. 89,5-91,5°C, Total yield, 46.6g (78%).

6.1.2.4 Preparation of Perfluorocyclohexene Oxide

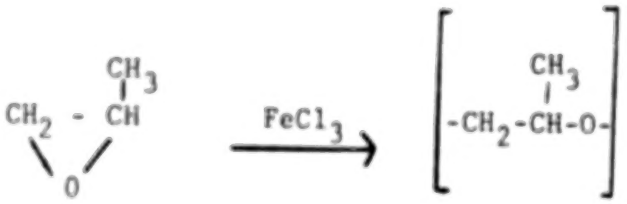
The techniques employed involved oxidation of perfluorocyclohexene with hydrogen peroxide (Ref. 219):



To a stirred solution of perfluorocyclohexene, 52,45g (0.2 mole), in anhdrous methanol, 50 ml, and with 30% hydrogen peroxide, 35 ml, was added 20% methanol-potassium hydroxide, 130 ml, over a period of 31/4 hours while maintaining temperature at -18 to -28°C in a dry ice-methanol bath. The reaction mixture was stirred in the cold bath for half an hour then brought to room temperature. The lower phase was separated and washed with water, dried and filtered. The recovered raw product, 25.57g, was fractionally distilled. The distillate was a clear liquid, 10.79g (19.39%), b.p. 52-55 (lit. 53-55), whose infrared spectrum showed characteristic oxide band at 6.7μ (Fig.4).

6.1.2.5 Polymerization of propylene oxide

Propylene oxide was polymerized to a high molecular weight polymer by using a catalytic complex.ferric chloride-propylene oxide (Ref. 220):



Ferric chloride - propylene oxide complex was prepared in a glass tube by adding propylene oxide, 0.514g (0.009 mole), to the cooled tube (-60°C) containing ferric chloride, 0.514g (0.003 mole), and 5 ml of ether while stirring with a magnetic stirrer. After half an hour at -60°C and half an hour at room temperature the ether was evaporated. The solid red complex was further dried under vacuum. To this tube was added propylene oxide, 60 ml (0.86 mole). The tube was heat-sealed under nitrogen while cooling in a dry ice-acetone bath. The tube was stirred to obtain a good mixture of the catalyst complex and the monomer, then placed in an oven for 90 hours at 83°C. The

reaction mixture was transferred to a 500 ml beaker with hot acetone. To this mixture, concentrated hydrochloric acid was added and the solution became clear. On standing overnight, a fluffy precipitate formed. The beaker was cooled in a dry ice-acetone bath and the precipitate was filtered. The precipitate was collected, redissolved in acetone with decolorizing carbon, filtered hot and reprecipitated twice through filter aid. A small amount of polymer was recovered, mp. 70°C (lit. 70°C), inherent viscosity of 1.01 dl/g (toluene, 26°C). The infrared spectrum of the polymer is shown in Fig. 5. The color of the polymer was yellow, indicating the presence of catalyst impurities.

Analysis: Calculated for C_3H_6O: C, 62.04; H, 10.42
Found: C, 62.08; H. 10.27

6.1.2.6 Polymerization of 1,1-dimethylethylene oxide

The ring opening polymerization of 1,1-dimethylethylene oxide was attempted by using boron trifluoride etherate as a catalyst (Ref. 218). Previously prepared dimethylethylene oxide (5 ml, 3.95g) was placed in a glass tube under nitrogen flow. The tube was cooled in dry ice-acetone. Redistilled boron trifluoride etherate (0.247g) was added to the tube with stirring. The tube was sealed and brought to room temperature. Polymer formation was negligible. A subsequent polymerization attempt was performed by using a catalytic system based on triethyl aluminum activated with cobalt acetylacetonate (Ref. 221).

1,1-dimethyethylene oxide, 3.97g (0.055 mole) was slowly added to a polymer tube charged with CO(acetylacetonate), 0.39g (0.0011 mole), and a solution of 5% triethyl aluminum in hexane, 15 ml (0.0044 mole), while stirring and flushing with nitrogen. After the addition, the polymer tube was chilled in liquid nitrogen, evacuated to 0.15 mm Hg

and sealed. Then the polymer tube was placed in a dry ice-acetone bath for 72 hours. The reaction mixture was precipitated in methanol, washed and dried under vacuum at 53°C. The recovered polymer, 0.61g, (yield 16%), exhibited a melting point of 158-161°C and was insoluble in common solvents. Films prepared from the melt turned opaque on cooling.

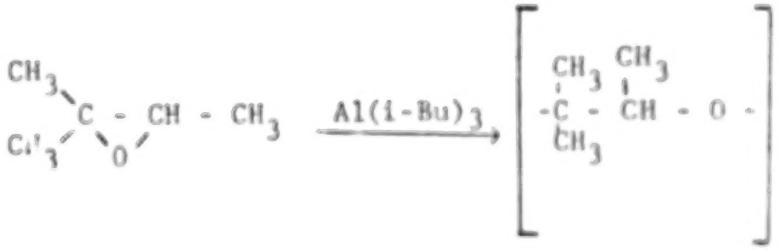
A third polymerization attempt was conducted by using a catalytic system based on triisobutylaluminum/water that was found to be effective in the polymerization of trimethylethylene oxide. The procedure used was as follows:

Methylene chloride (30 ml) was added under nitrogen to a 100 ml flask fitted with a rubber septum. Triisobutylaluminum (0.5 ml) and distilled water (0.018 ml) was injected with a microsyringe while cooling in ice bath and stirring. The flask was then cooled in a dry ice-acetone bath and 1,1-dimethylethylene oxide, 4.5 ml (3.58g, 0.05 mole), was injected while vigorously stirring. The reaction mixture was allowed to stand in dry ice-acetone bath overnight. The methylene chloride was evaporated and the product precipitated with water, filtered, washed with methanol and dried under vacuum at 50°C. The yield was 0.29g (8.1%). The polymer had poor film-forming properties. The melting point, determined on a Fisher-Jones apparatus, was 160-163°C. The infrared spectrum of this polymer is shown in Fig. 6.

Analysis: Calculated for C_4H_8O: C, 66.63; H. 11.18
Found: C, 66.39; H. 11.08

6.1.2.7 Polymerization of trimethylethylene oxide

This polymerization was performed by using triisobutylaluminum/water as the catalyst, as reported by Field and co-workers (Ref.222):



Methylene chloride, 30 ml, was added to a flask cooled with ice and equipped with a rubber septum, nitrogen inlet and outlet. Triisobutylaluminum, 0.5 ml (0 002 mole), and distilled water, 0.018 ml, were injected into the flask. After aging overnight at room temperature, the flask was cooled in a dry ice-acetone bath, and trimethylethylene oxide, 5 ml (0.05 mole), was added with a syringe. Immediate polymerization took place. The reaction mixture was precipitated with a methanol-HCl solution. The precipitate was collected, washed with methanol and dried under vacuum at 53°C. The polymer yield was 3.15g (73.0%). m.p. 166-170, inherenet viscosity 0.18 (toluene, 26°C). The infrared spectrum of this polymer is show in Fig. 7.

Analysis: Calculated for $C_5H_{10}O$: C, 69.72: H, 11.70
Found: C, 69.56; H, 11.71

6.1.2.8. Polymerization of tetramethylethylene oxide

The polymerization was conducted by using boron trifluoride etherate as the catalyst (Ref 220,223)

Methyl chloride (100 ml) was liquified in a glass tube flushed with nitrogen and cooled with dry ice-acetone. Tetramethylethylene oxide (5 ml) was added to the glass tube while purging with nitrogen. To this solution was added redistilled boron trifluoride etherate (1 ml). The solution turned almost instantly into a thick gel. The mixuture was allowed to stand at dry ice temperature for 24 hours. A small volume of methylene chloride was added, the polymer was filtered, washed with methanol and dried. The polymer obtained was a white solid with unusual thermal and solvent resistance. It did not melt or discolor even at 400°C. It was only slightly soluble in boiling trichlorobenzene or benzyl alcohol. It was soluble in concentrated sulfuric acid or trifluoroacetic acid but polymer degradation took place in these solvents.

Analysis: Calculated for $C_6H_{12}O$: C,71.95; H. 12.08
Found: C, 71.39; H, 11.97

In the attempt of obtaining a more tractable polymer, the use of triisobutyl aluminum - water as the polymerization catalyst,was investigated. The resulting polymer exhibited the same characteristics of insolubility and infusibility. The procedure employed was similar to the one employed for the polymerization of trimethylethylene oxide.

Methylene chloride, 30 ml, was added to a flask cooled with ice and equipped with a rubber septum, nitrogen inlet and outlet. Tri-isobutyl aluminum, 0.5 ml (0.39g, 0.002 mole), and distilled water, 0 018 ml (0.001 mole) was injected with a microsyringe. After aging the catalyst overnight at room temperature, the flask was cooled in a dry ice-acetone bath and tetramethylethylene oxide, 6 ml (4.98g, .0497 mole), was added. After one hour, the flask was removed from the dry ice-acetone bath and the reaction mixture was precipitated with methanol-HCl twice in a Waring blender. After washing with methanol, filtering and drying under vacuum, a white solid polymer was recovered that was infusible and insoluble in all common solvents. The infrared spectrum of this polymer is shown in Fig. 8.

Analysis: Calculated for $C_6H_{12}O$: C, 71.95; H. 12.08
Found: C, 71.98; H, 12.16

6.1.2.9. Copolymerization of trimethylethylene oxide and tetramethylethylene oxide.

The procedure was essentially identical to the homopolymerization of tetramethyl - and trimethylethylene oxide with tri-isbutyl aluminum - water catalyst. Equimolar amounts of the two monomers was employed for copolymerization (0.025 mole each). The recovered white polymer (3.36g; yield, 72%) exhibited the same characteristics of infusibility and insolubility as the homopolymer of tetramethylethylene oxide. The infared spectrum of this polymer is shown in Fig 9.

Analysis: Calculated for the Copolymer $C_{11}H_{22}O_2$: C,70.92;

H, 11.91

Found: C, 70.70; H, 11.96

6.1.2.10 Polymerization of Cyclohexene oxide

The technique employed was based on the method of Bacskay (Ref. 224:

Triethyl aluminum (1 ml) in n-hexane (100 ml) was added to a 500 ml flask equipped with thermometer, mechanical stirrer and dropping funnel. The flask was purged with nitrogen and cooled in a dry ice-acetone bath. Cyclohexene oxide (20g) was added slowly to the stirred catalyst solution. A gummy, white polymer precipiated instantly upon contact of the monomer with the catalyst solution. After completing the addition, a mixture of methanol and concentrated HCl was added to the flask to decompose and dissolve the unreacted catalyst. The reaction product was dissolved in benzene and coagulated in excess of methanol. This was repeated twice. The white, ubbery polymer was washed with methanol in a blender, filtered and dried under vacuum. A white polymer was isolated, m.p. 150 - 168°C, inherent viscosity 0.76 dl/g (toluene, 26°C). The yield was 5.87g (24%). The carbon analysis was 1% too high as compared to the calculated amount, indicating the presence of impurities. The infrared spectrum of this polymer is shown in Fig 10.

Analysis: Calculated for $C_6H_{10}O$: C,73.43; H, 10.29

Found: C, 74.44; H, 10.16

6.1.2.11 Attempted polymerization of perfluorocyclohexene oxide

The successful polymerization of cyclohexene oxide with organometallic catalysts led us to attempting the polymerization of the perfluorinated analog.

Perfluorocyclohexene oxide, 4.32g (0.016 mole), was injected into a septum sealed flask charged with triethyl aluminum, 0.07 ml (0.52

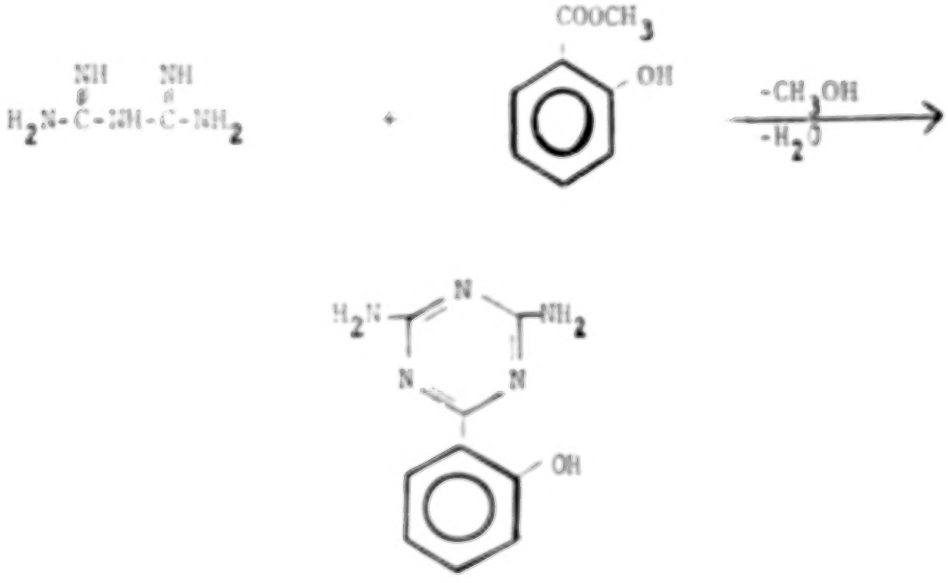
mole) in hexane, 20 ml, while cooling in a dry ice-acetone bath and vigorously stirring for 18 hours. Polymer formation was not observed. Other catalytic systems have not been investigated.

6.1.3. Guanamine Resins

Butylated guanamine/formaldehyde resins suitable for coating application were prepared by reaction with paraformaldehyde in n-butanol according to known methods (Ref. 225).

6.1.3.1 Preparation of o-hydroxybenzoguanamine

The method employed involves the condensation of biguanide with methylsalicylate (Ref 226):



A saturated solution of biguanide in methanol was prepared by dissolving 25.5g biguanide in 100 ml of methanol while heating in a warm water bath. The solution was cooled and filtered. Methylsalicylate (44g) was added to this solution. After standing for four days the hydroxybenzoguanamine had precipitated as small light yellow crystals. This was recrystallized from a 50/50 mixture of water/ethyl ether of ethyleneglycol The isolated product was dissolved in ethyl ether of ethylene glycol and reprecipitated in water. The light yellow precipitate was filtered, washed with water and dried under vacuum. The yield was 6g of o-hydroxybenzoguanamine.

6.1.3.2 Polymerization of Benzoguanamine with Formaldehyde

A test tube containing paraformaldehyde, 0.9g (0.03 mole), benzoguanamine, 1.87g (0.01 mole), and 5 ml of n-butanol was heated under reflux until a clear solution was obtained. To this solution, a catalytic amount of concentrated hydrochloric acid, 0.0025 ml, was added and heating was continued while a water/butanol azeotrope and most of the butanol present in excess were distilled leaving a viscous resin solution. This was dissolved in ether, washed with 2.5% sodium hydroxide, then with water. The organic phase was dried, filtered and concentrated. A solution of this resin in n-butanol was utilized for coating.

6.1.3.3 Polymerization of O-Hydroxybenzoguanamine with Formaldehyde

The polymerization was carried out in a test tube containing paraformaldehyde, 0.9205g (0.031 mole), o-hydroxybenzoguanamine, 2.0491 (0.010 mole) and 5 ml of n-butanol. The mixture was heated and mixed until a clear solution was obtained. Concentrated hydrochloric acid, 0.0025 ml, was added to the solution and heating continued while water/butanol azeotrope and excess butanol were distilled. The resulting resin was dissolved in ether, washed with dilute base, then with water. The organic phase was dried and concentrated. The recovered resin was dissolved in 10 ml of n-butanol and utilized for coating. The infrared spectrum of this polymer revealed the presence of traces of carbonyl group (5.8μ) probably due to oxidation during polymerization or curing (Fig. 11).

6.1.3.4 Copolymerization of Benzoguanamine/O-Hydroxybenzoguanamine/Formaldehyde

Copolymers were prepared at molar ratios benzoguanamine/o-hydroxybenzoguanamine of 98/2 and 50/50.

A mixture of benzoguanamine, 1.835g (0.0098 mole), o-hydroxybenzoguanamine, 0.041g (0.0002 mole), paraformaldehyde, 0.90g (0.03 mole), and 7 ml of butanol was heated in a test tube until a clear solution appeared. A catalytic amount of concentrated hydrochloric acid, 0.0025 ml, was injected into the clear solution. The solution was allowed to boil and distill to a small volume. The cooled product was dissolved in ether and washed with 2% sodium hydroxide then with water. A 20% butanol solution of this copolymer was utilized for coating.

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A polymer from benzoguanamine, 0.94g (0.005 mole), o-hydroxybenzoguanamine, 1.002g (0.005 mole), and paraformaldehyde, 0.9g (0.03 mole) was prepared in this same manner.

6.2 Preparation of Coatings for Testing

6.2.1 Polypivalolactone

The material employed was supplied by the du Pont Co. The polymer was a white powder with an inherent viscosity of 1.38 (0.5% in trifluoracetic acid at 25°C) and a melting point of 235°C. Because of the insolubility of this material, a melt method was employed. Polypivalolactone powder was placed on the aluminum coupon and melted at 250 - 260°C under nitrogen. A glass slide was placed over the melt to obtain a smooth surface. The coating was rapidly quenched in dry ice to prevent crystallization.

6.2.2 Neopentylglycol Polycarbonate

A 5% solution in dichloroethane was spread over the coupon and allowed to evaporate at 50°C. The temperature was gradually increased up to the softening temperature of the polycarbonate (110°C). This procedure allowed the formation of clear films. The coupon was gradually cooled and removed from the hot bench heater.

6.2.3 Polyvinylcarbazole

Polyvinylcarbazole (Aldrich analyzed, Mn=276,000, Mw=1,410,000) was dissolved in chlorobenzene (3%) and the solution applied to the surface of the coupon. The coating was slowly dried at room temperature under a glass funnel. After overnight drying, vacuum was applied with a diffusion pump to assure solvent removal. A clear, smooth film was obtained.

6.2.4 Polyvinylnaphthalene

Polyvinylnaphthalene (Polyscience, Inc.) was purified by dissolving the polymer in distilled toluene and coagulating the solution in excess of methanol. The precipitate was filtered, washed with methanol, and dried. This procedure was repeated three times. The color of the polymer was greatly improved by purification. After the third reprecipitation the polymer was almost colorless. The purified material was dissolved in distilled toluene (2% - wt). The coated coupons were dried at 90°C and further dried under vacuum.

6.2.5 Poly(ethylene Oxide)

A 0.15% methylene chloride solution of poly(ethylene oxide) was spread over the substrate and the solvent evaporated at room temperature. After evaporation of the solvent at 70°C, the coupon was placed in a drying apparatus which was heated with refluxing methylene chloride and evaporated to 1mm Hg for 17 hours.

6.2.6 Poly(trimethylethylene Oxide)

A 10% benzene solution of poly(trimethylethylene oxide) was spread over the substrate and the solvent allowed to evaporate at 60°C. Then it was placed on a hot plate at 200°C until the film softened into a clear melt which was immediately quenched in an ice bath to form a clear, hard film.

6.2.7 Poly(cyclohexene Oxide)

A 10% benzene solution of poly(cyclohexene oxide) was spread over the substrate, allowed to dry under a glass funnel overnight, and further dried under vacuum at 0.2 mm Hg. A clear, transparent film was obtained.

6.2.8 Guanamine/Formaldehyde Resins

The polymers obtained from benzoguanamine/formaldehyde, o-hydroxybenzoguanamine/formaldehyde, and the copolymers of benzoguanamine/o-hydroxbenzoguanamine/formaldehyde were coated according to the following general procedure:

A 15% solution of the resin in n-butanol was spread over the substrate and dried in an oven for four hours at 80°C. Curing was performed by increasing the temperature to 150°C overnight under nitrogen flow. Transparent, hard films were obtained.

6.3 Irradiation of Coatings and Reflectance Measurements

The ultraviolet irradiation studies were conducted at the Langley Research Center. A modular ultraviolet irradiation system, shown in Fig. 12 and described in Ref. 227, was used to irradiate these polymers and measure their spectral reflectance in situ, under high vacuum conditions. The test polymers were cast on 2.5 cm-diameter aluminum discs which were highly polished to 1 μm. During irradiation testing, the samples were mounted on a water cooled base in individual stainless-steel vacuum chambers, Fig. 13, each equipped with a 25-l/sec ionization pump. Six of these vacuum chambers are located around a central housing containing an air cooled 1000-watt xenon arc lamp. Radiation from the zenon lamp is focused on the front surface of the test sample by a movable lens mounted in an optical path extending radially from the lamp housing. This focusing lens can vary the intensity of the radiation incident upon the test sample from 0.5 to 5.0 equivalent ultraviolet solar constants. The intensity used for these tests was 1.0 solar constants. The pressure during these tests was less than 1.33×10^{-5} Pa (1×10^{-7} torr).

The test sample is mounted on a high-vacuum push-pull feed-through which is used to manipulate the test sample in the vacuum chamber from the ultraviolet-exposure position, behind a quartz window, to the reflectance measurement position in a quartz tube extending from the base of the vacuum chamber. When a spectral reflectance measurement was to be made in situ, the test-sample vacuum chamber was placed on a specially designed integrating sphere with the quartz tube projecting into the center of the sphere. The sample was moved into the quartz tube by use of the feedthrough, and the spectral reflectance measurement performed without exposing the sample to air. A spectral calibration is used to correct for the effects of the quartz tube on the spectral reflectance of the test sample. The spectral reflectance measurements were performed over the wavelength range from 0.25 μm to 2.65 μm.

7. CONCLUSION

A literature review in the field of ultraviolet and charged particle effects on polymers has been utilized as a basis for an experimental program aimed at the development of radiation stable materials for space applications. Synthesis, characterization and ultraviolet radiation exposure tests have been performed on several materials selected for study on the basis of structual considerations.

A study of the photolysis of polyvinylcarbazole indicated initial good stability, but the rate of degradation increased with increasing the radiation dose, causing reflectance degradation both in the UV and visible region.

Unlike polyvinylcarbazole, polyvinylnaphthalene exhibited some radiation damage during the first 1100 hours of irradiation, but essentially no damage for subsequent doses. Because of its aromatic structure combined with a low value of α_s, polyvinylnaphthalene is a promising candidate for combined environment.

A study of the photolysis of aliphatic polyester and polycarbonate structures in which photodegradation via Norrish type II was prevented by disubstitution of the carbon atom in β-position with respect to the in-chain oxygen link led to the conclusion that preventing the energetically favored Norrish type II improves polymer stability but is not sufficient to provide long-term radiation resistance.

A study of amino resins incorporating o-hydroxybenzoguanamine as a UV stabilizer/comonomer seemed to indicate that polymer stability increases with increasing o-hydroxybenzoguanamine concentration but the relationship between UV stability and amino resin compositions was not clear. The ultraviolet stability may have been affected by the presence of traces of carbonyl groups, that were detected by infrared analysis.

Irradiation of poly(ethylene oxide) confirmed previous observations that this material possesses excellent stability to ultraviolet irradiation in vacuum. The unusual aspect of the photolysis

of poly(ethylene oxide) is that irradiation does not cause optical damage but rather an improvement in reflectance as indicated by values of α_s that decrease with increasing exposure time.

Other aliphatic polyethers tested by UV irradiation were less stable than poly(ethylene oxide). Irradiation of poly(trimethylethylene oxide) showed an improvement in reflectance in the IR region in conjunction with reflectance degradation in the UV and visible region. The low ultraviolet stability of poly(cyclohexene oxide) was disappointing in view of the good film-forming properties of this material. The observation that the carbon content of the poly(cyclohexene oxide) tested was higher than the calculated value suggests that additional synthesis work should be performed on this polymer to determine whether the presence of impurities was responsible for the observed instability.

In conclusion, of the several materials that have been examined in this study, the most promising appear to be polyethylene oxide, polyvinylnaphthalene, and the amino resin prepared by the condensation of o-hydroxybenzoguanamine with formaldehyde. Further work is anticipated to determine the applicability of these materials as metallized films for second surface mirrors, and to further investigate their properties both from the standpoint of performance and scale-up potential.

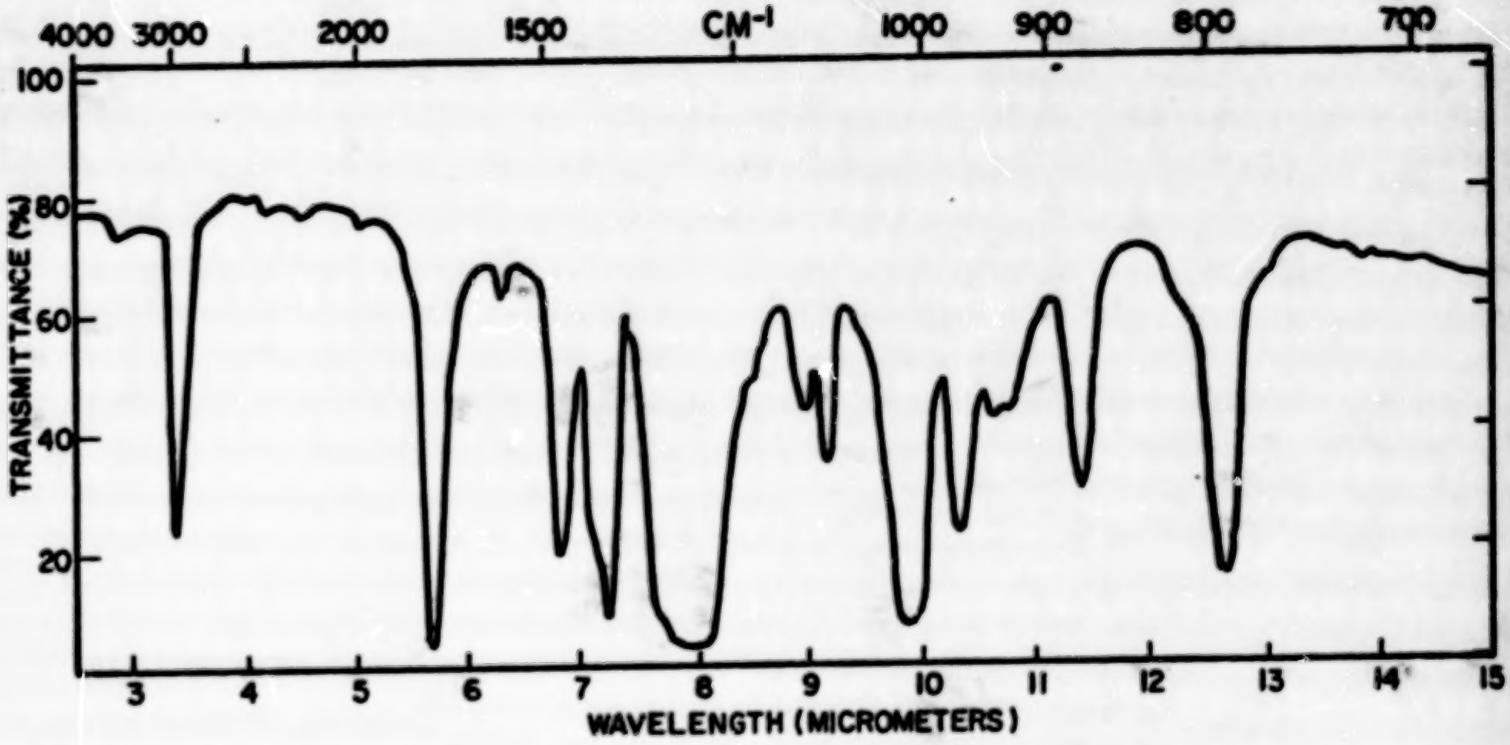

Figure 1: IR SPECTRUM OF NEOPENTYLGLYCOL-BIS-(ETHYLCARBONATE)

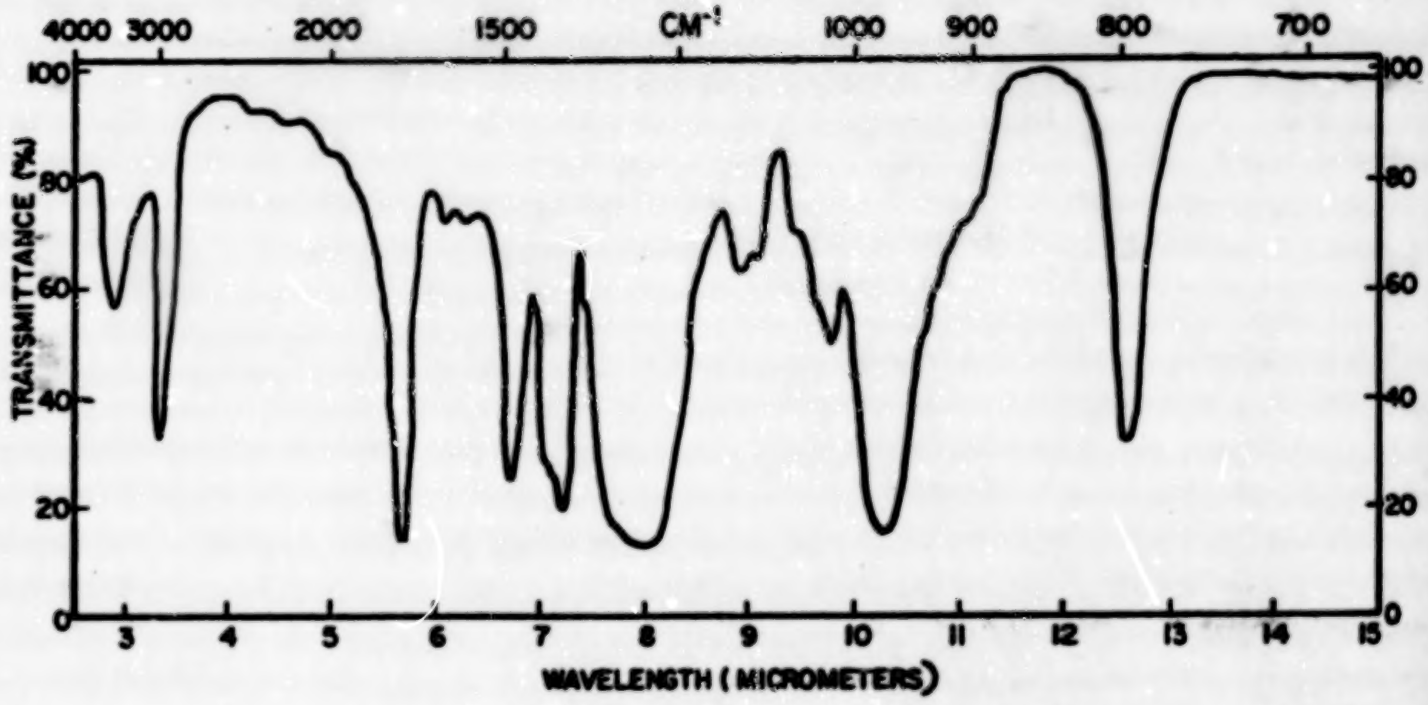

Figure 2: IR SPECTRUM OF NEOPENTYLGLYCOL POLYCARBONATE

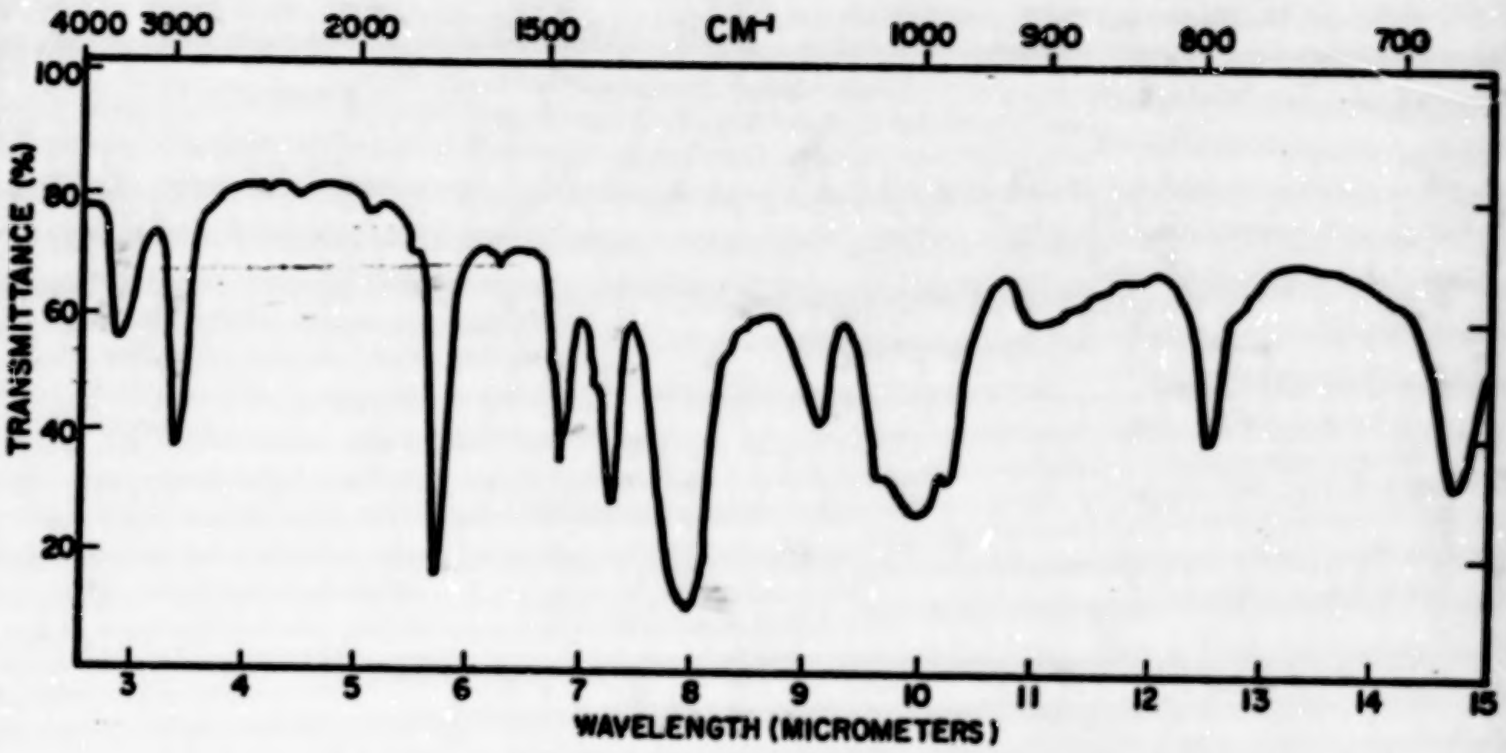

Figure 3: IR SPECTRUM OF TETRAMETHYLCYCLOBUTANEDIOL POLYCARBONATE

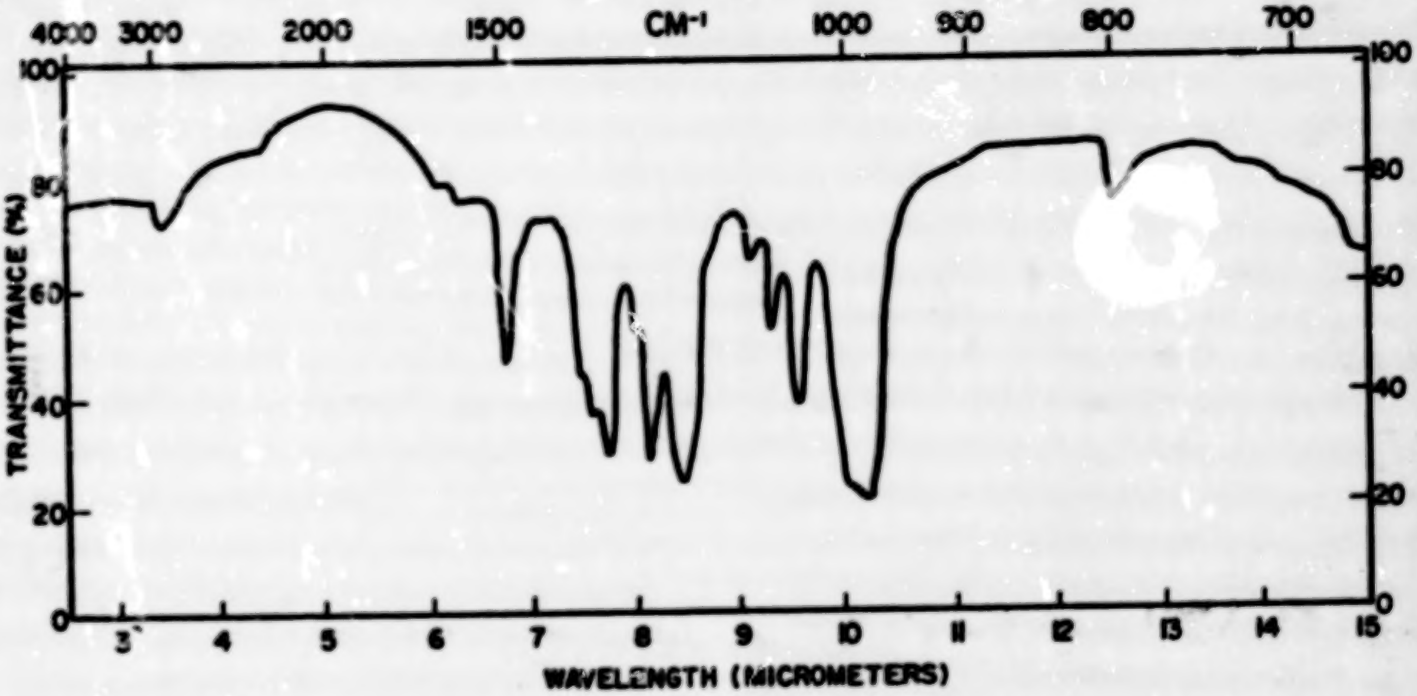

Figure 4: IR SPECTRUM OF PERFLUOROCYCLOHEXENE OXIDE

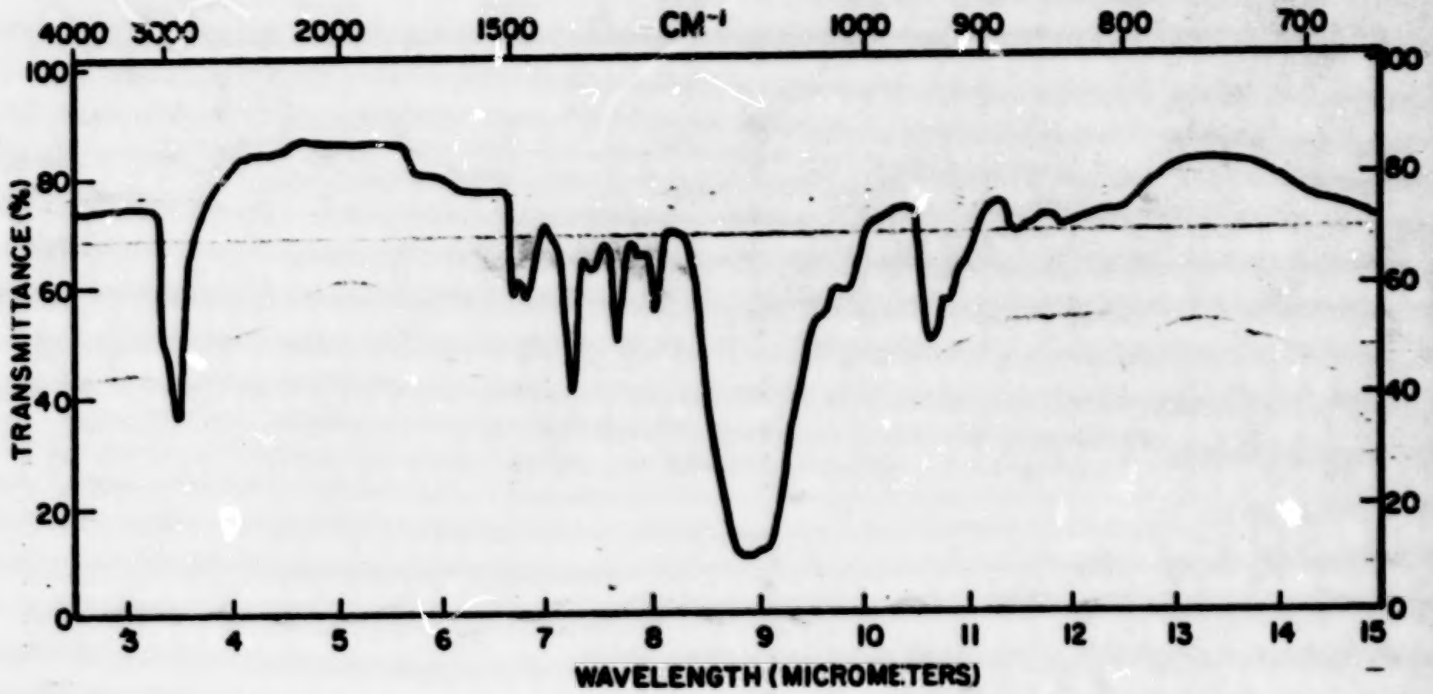

Figure 5: IR SPECTRUM OF POLYPROPYLENE OXIDE

100

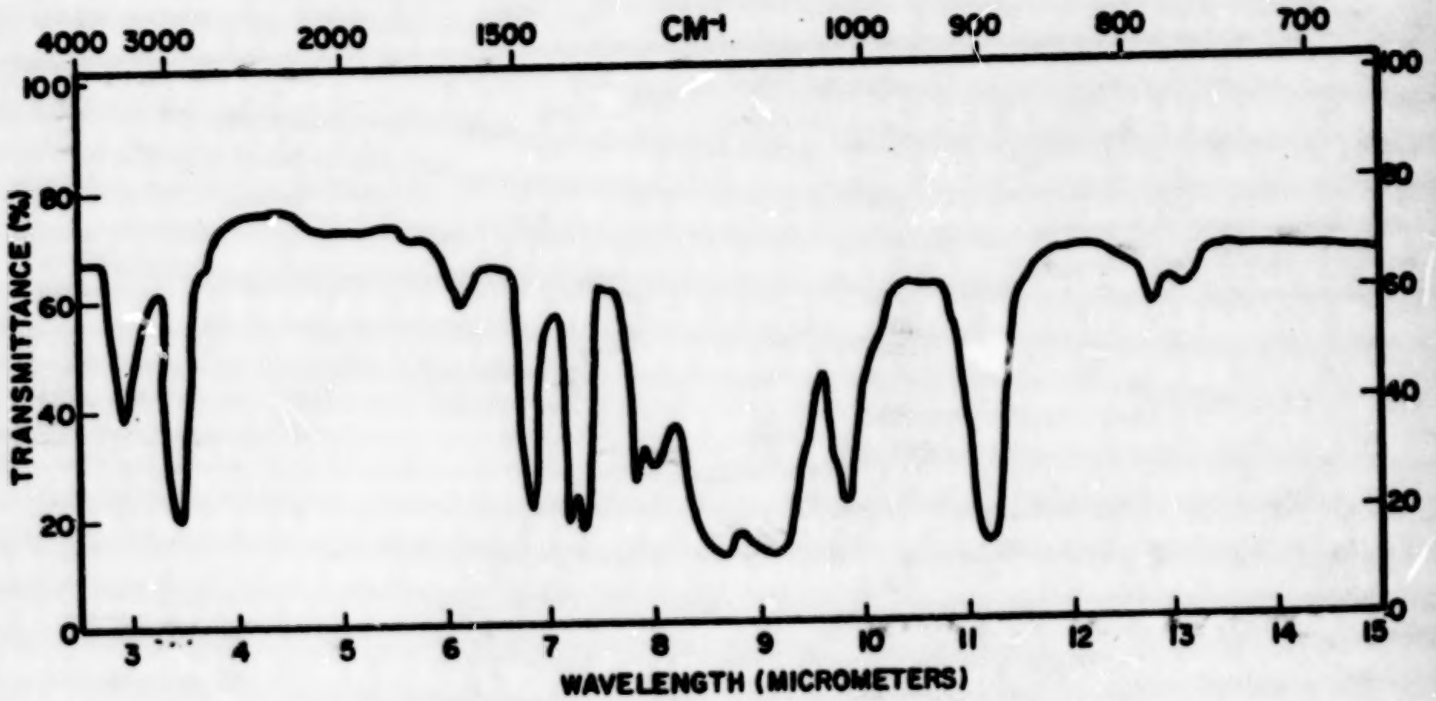

Figure 6: IR SPECTRUM OF POLY(DIMETHYLETHYLENE OXIDE)

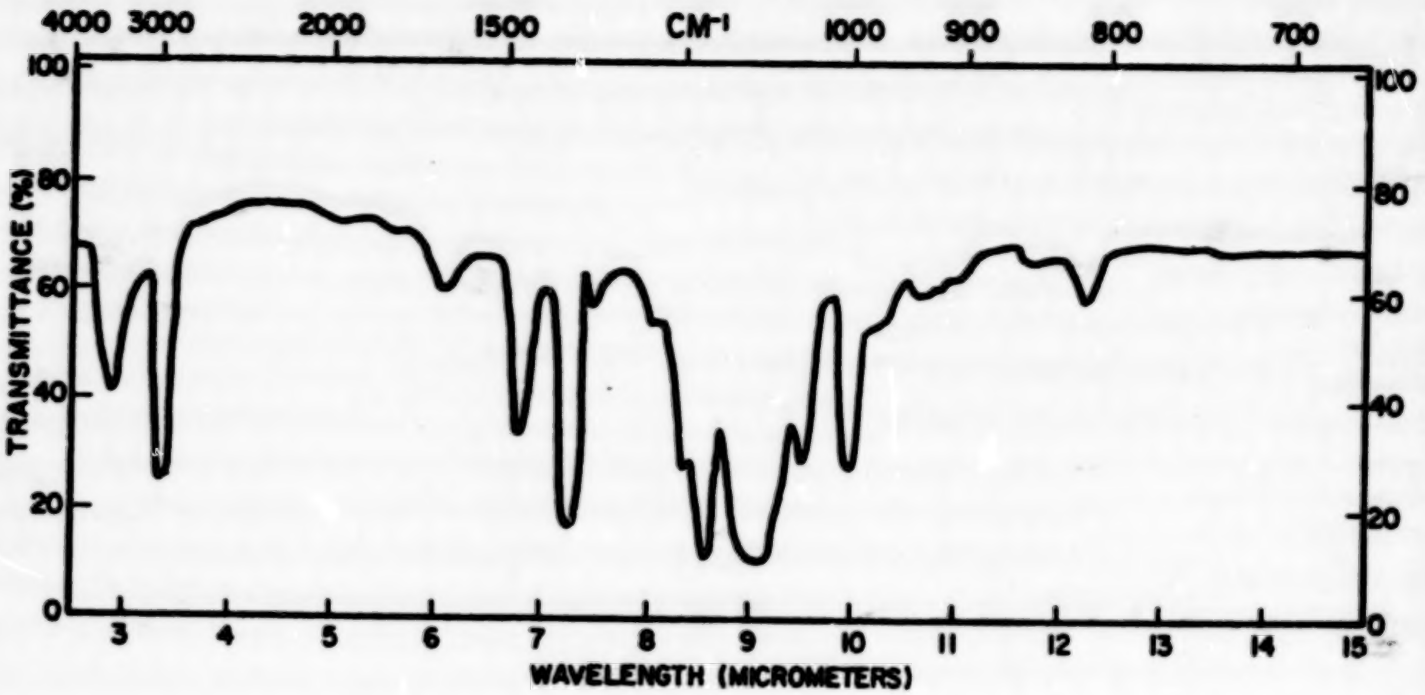

Figure 7: IR SPECTRUM OF POL(TRIMETHYLETHYLENE OXIDE)

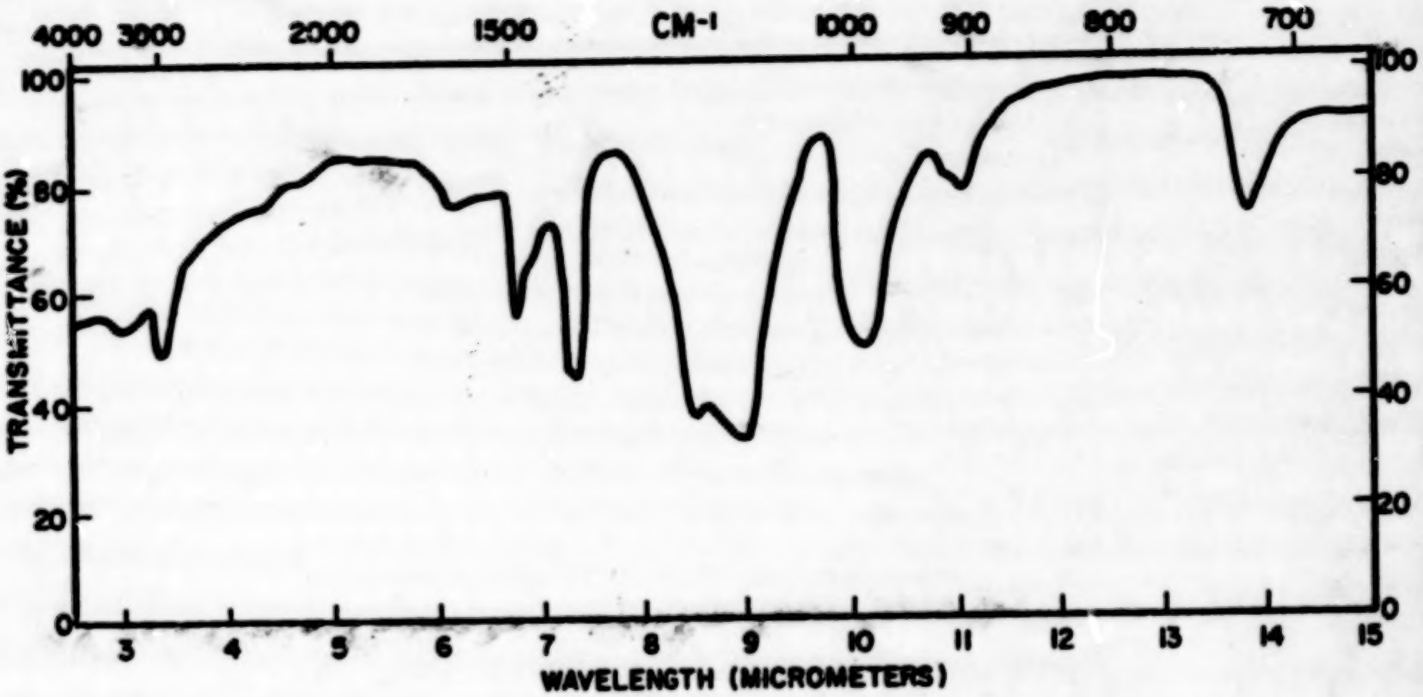

Figure 8: IR SPECTRUM OF POLY(TETRAMETHYLETHYLENE OXIDE)

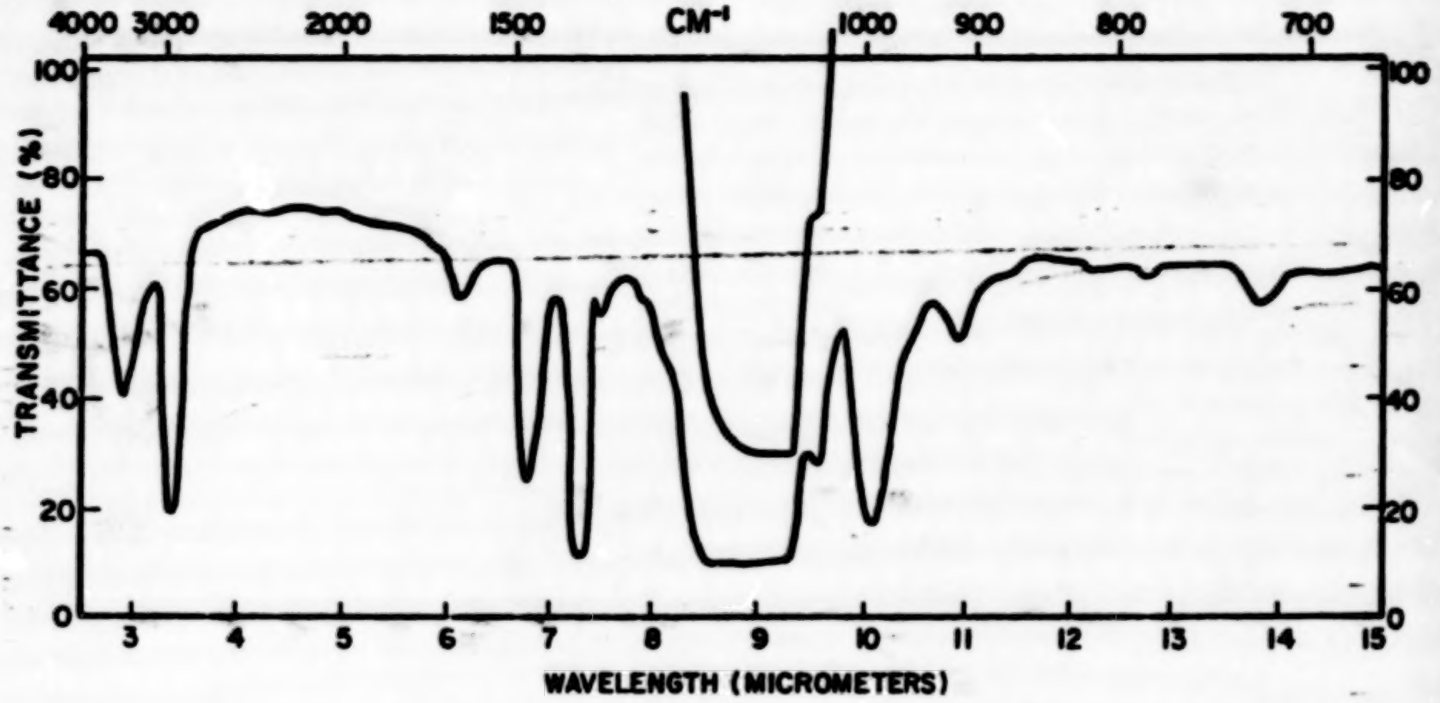

Figure 9: IR SPECTRUM OF THE COPOLYMER OF TRIMETHYL-AND TETRAMETHYL-ETHYLENE OXIDE

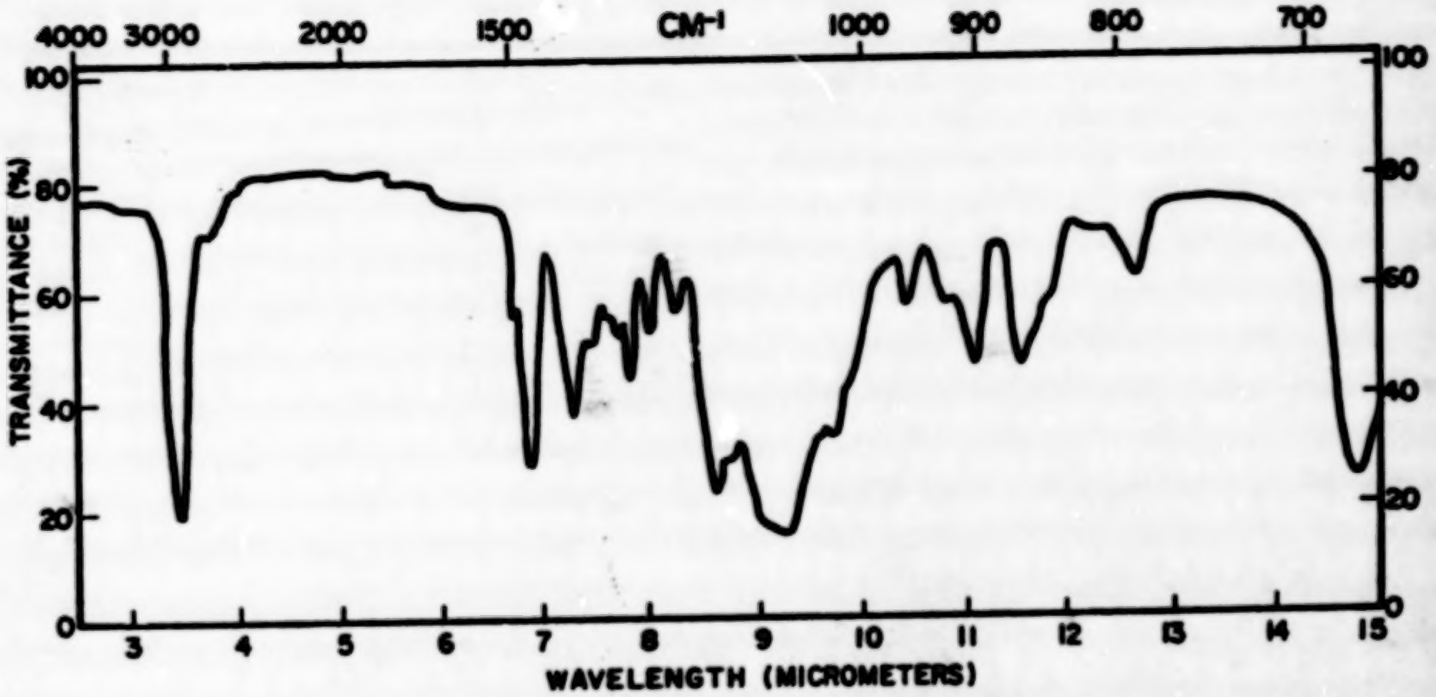

Figure 10: IR SPECTRUM OF POLYCYCLOHEXENE OXIDE

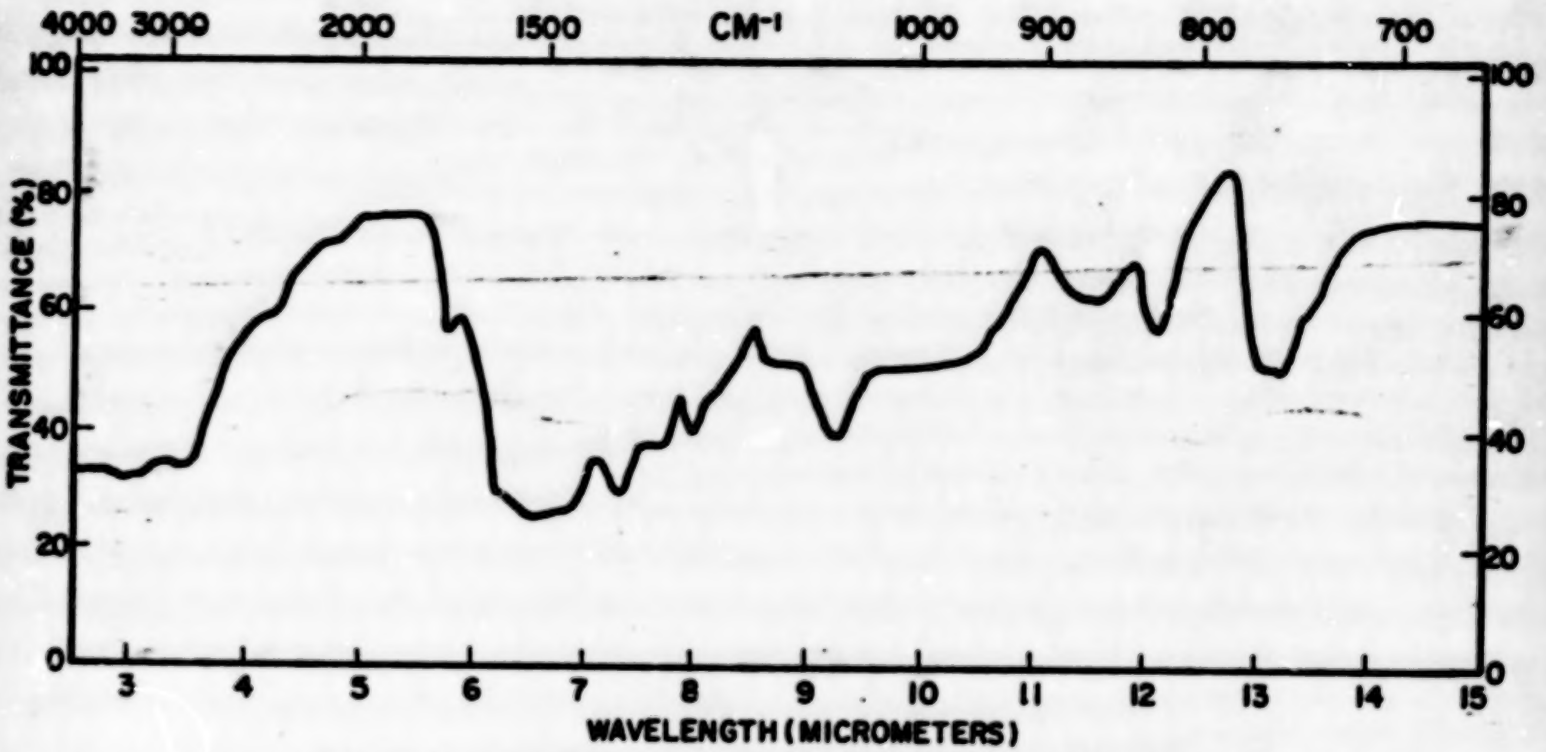

Figure 11: IR SPECTRUM OF O-HYDROXYBENZOGUANAMINE/FORMALDEHYDE RESIN

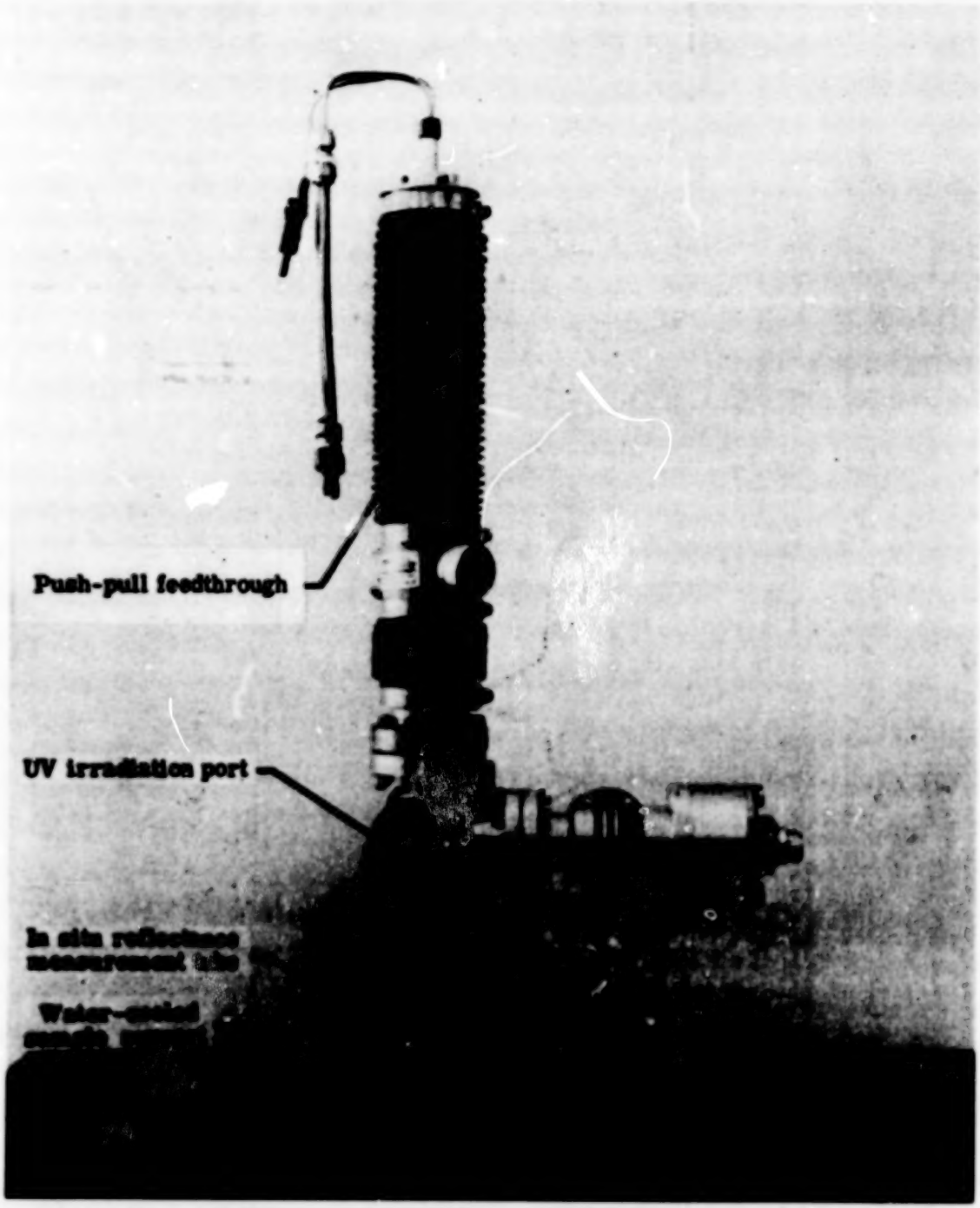

Figure 12: Test-sample vacuum chamber.

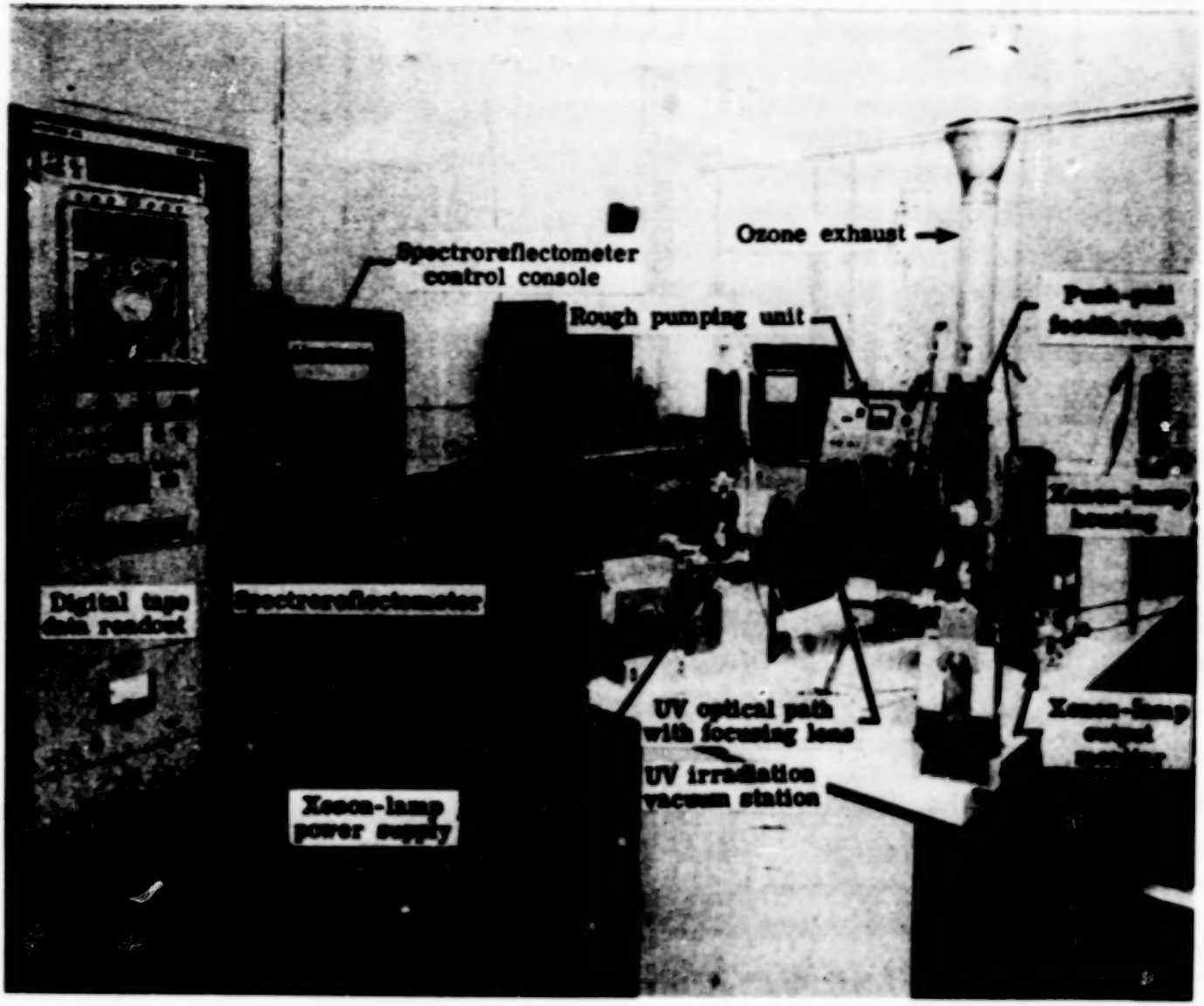

Figure 13: UV irradiation apparatus and in situ reflectance measurement system.

APPENDIX

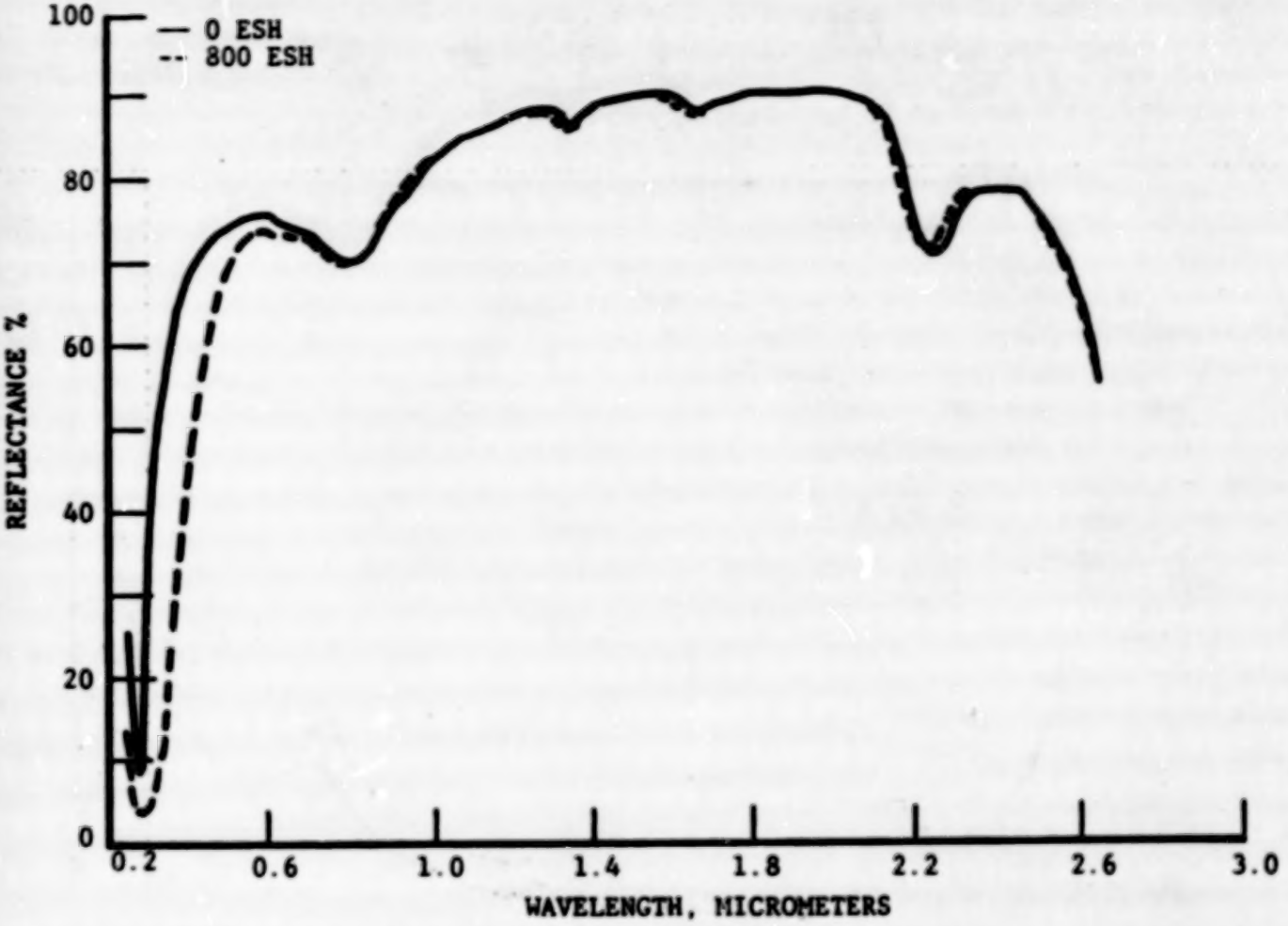

Fig. A-1 Effect of UV Irradiation on the Reflectance of Polypivalolactone

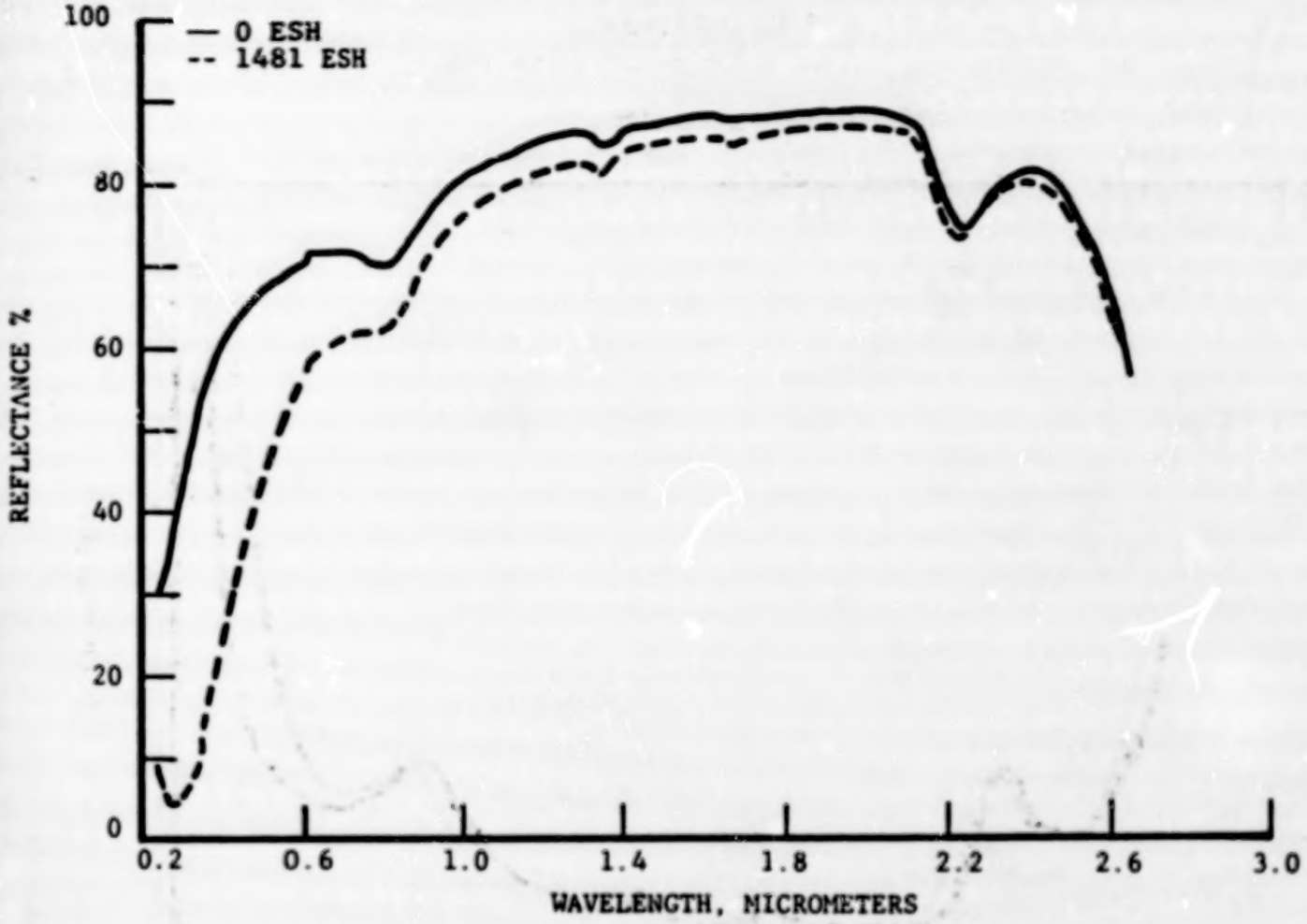

Fig. A-2 Effect of UV Irradiation on the Reflectance of Neopentylglycol Polycarbonate

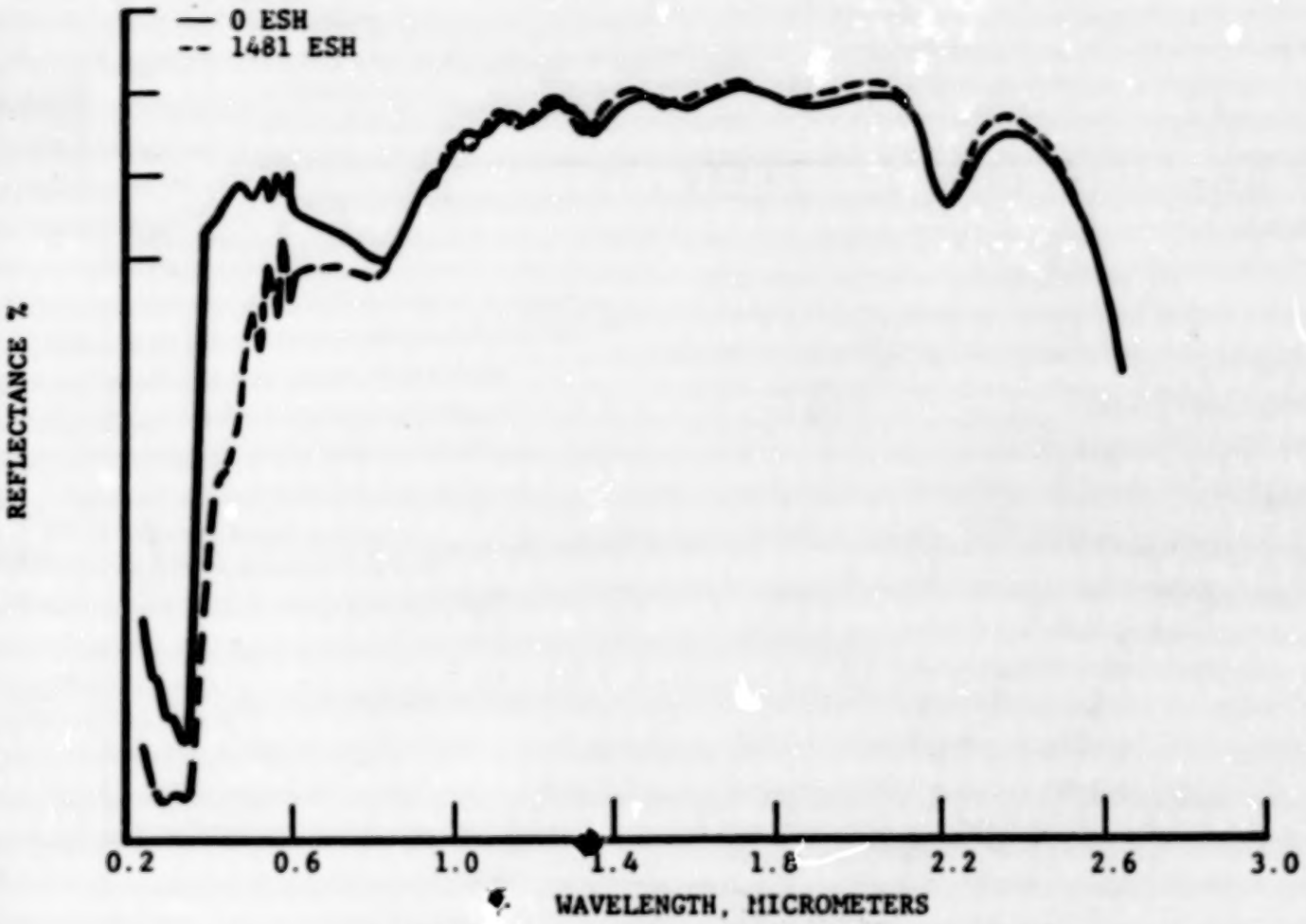

Fig. A-3 Effect of UV Irradiation on the Reflectance of Polyvinylcarbazole (1st sample)

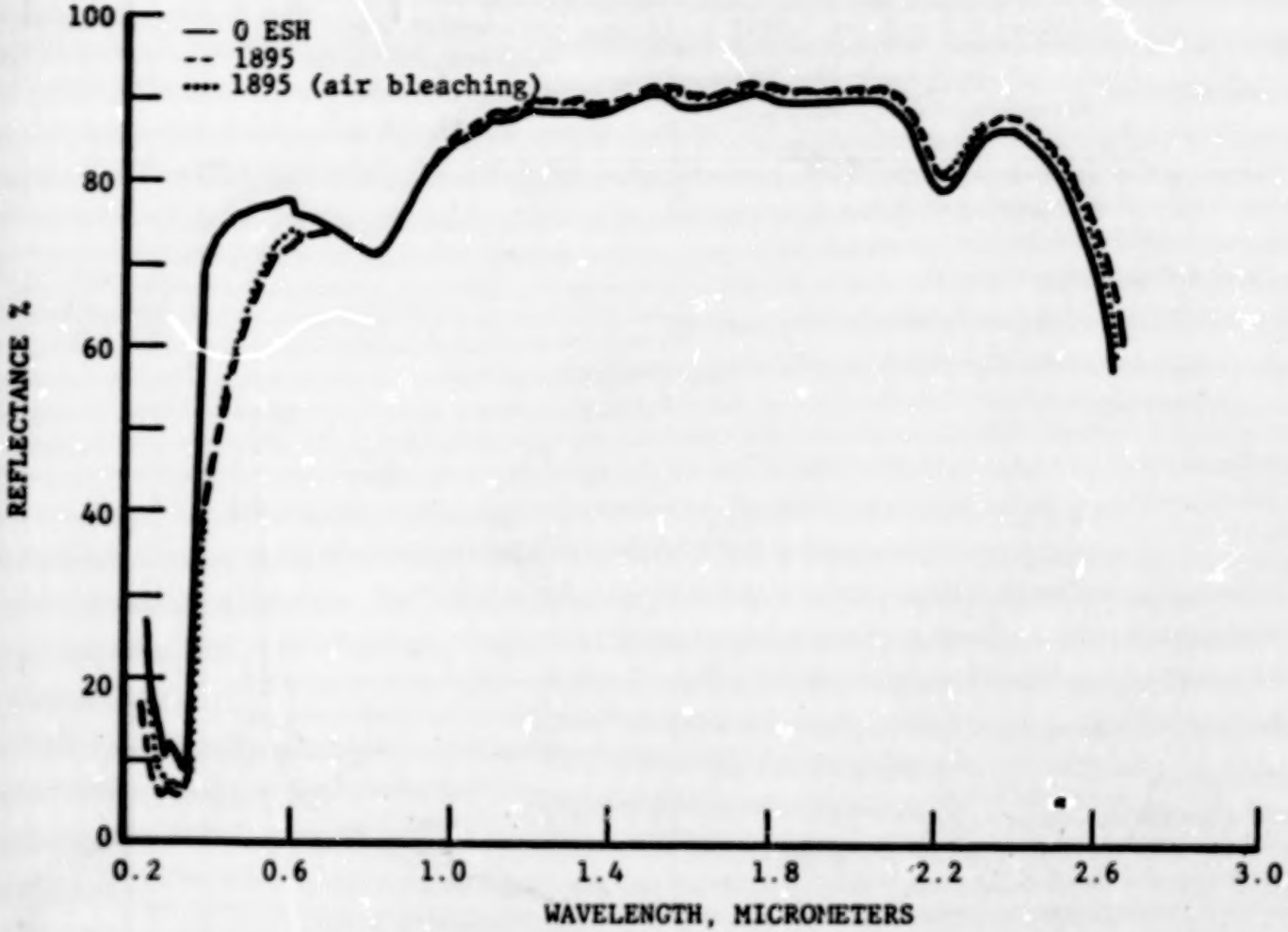

Fig. A-4 Effect of UV Irradiation on the Reflectance of Polyvinylcarbazole (2nd sample)

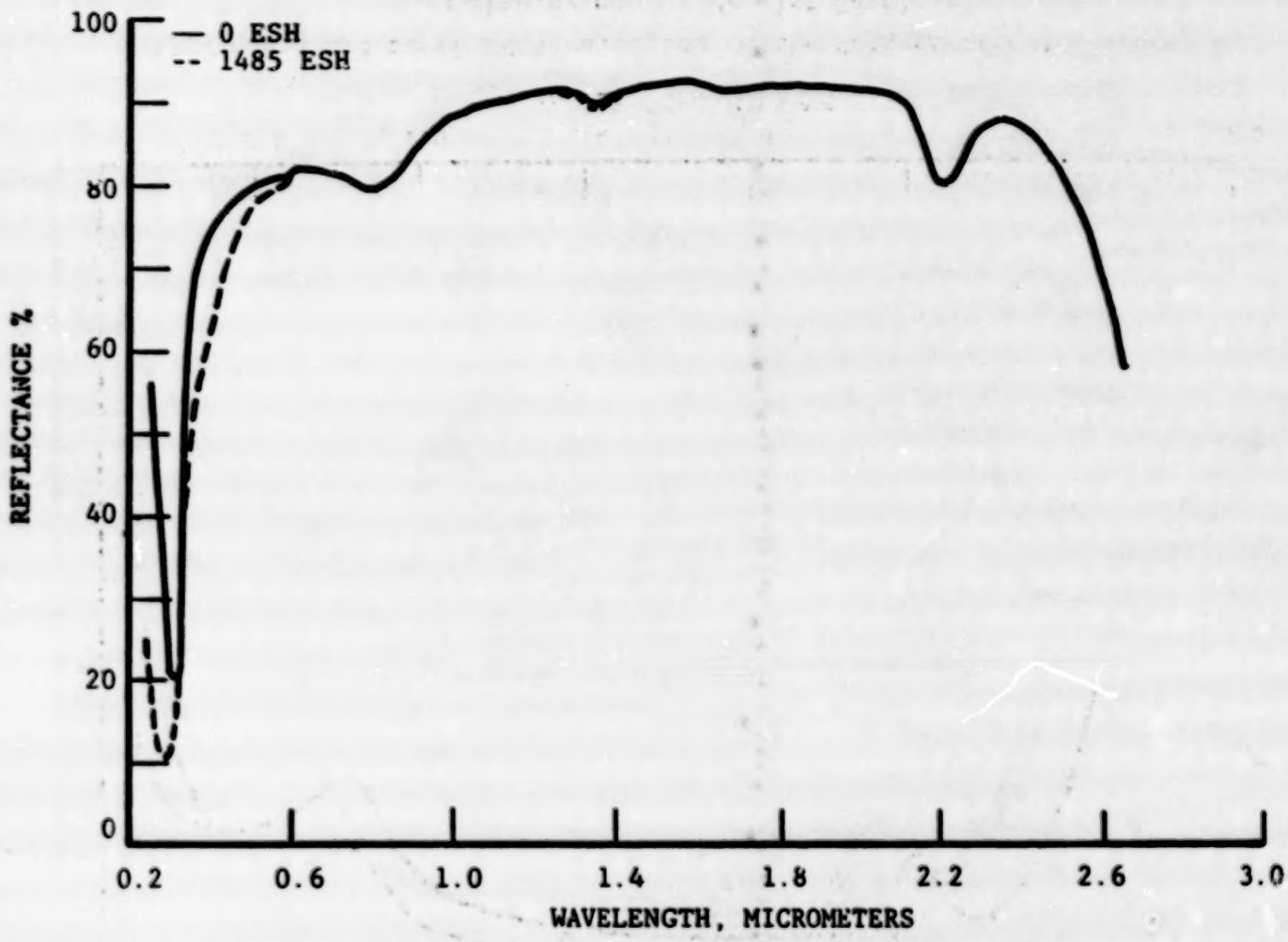

Fig. A-5 Effect of UV Irradiation on the Reflectance of Polyvinylnaphthalene (2nd Sample)

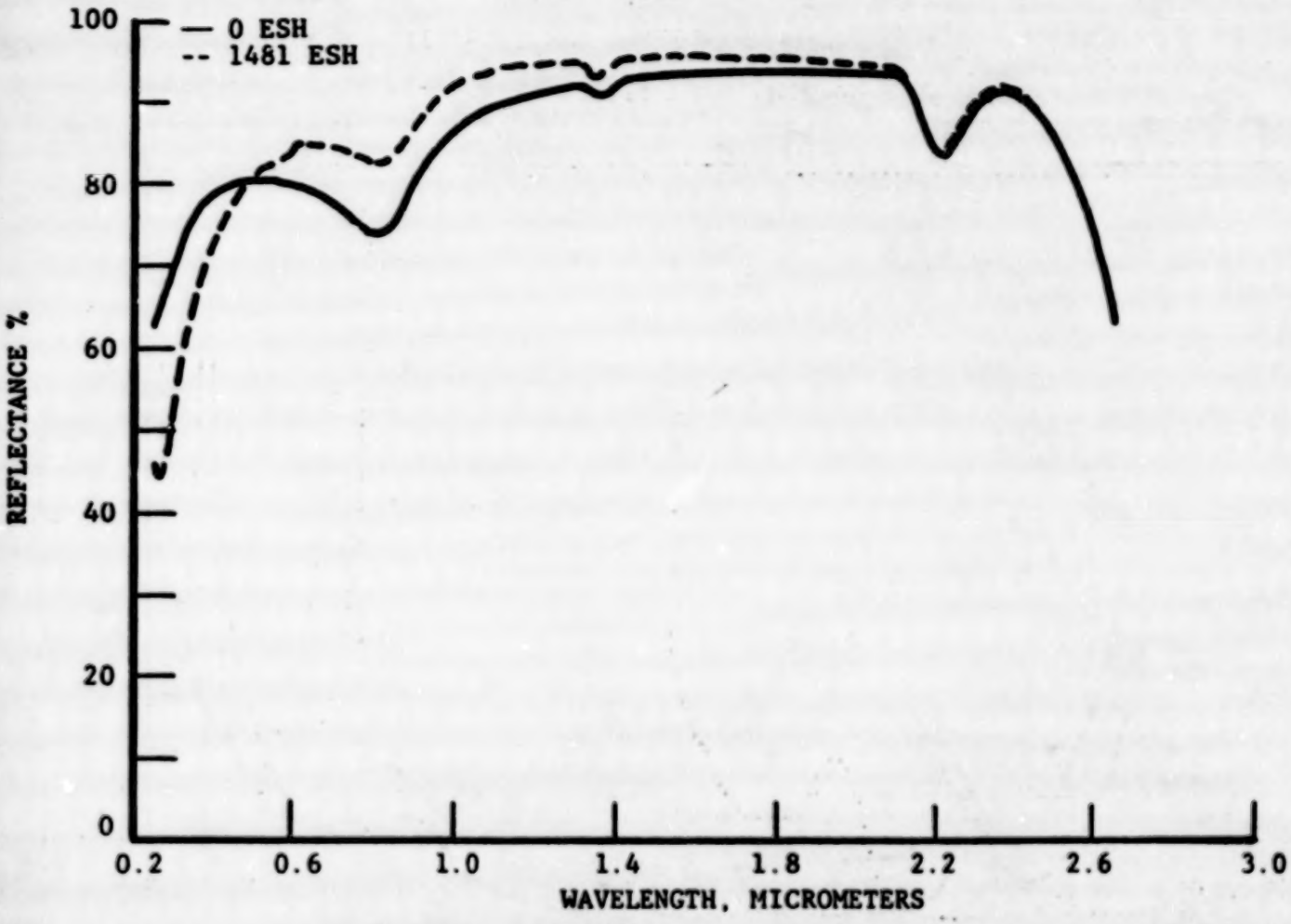

Fig. A-6 Effect of UV Irradiation on the Reflectance of Polyethylene Oxide (1st Sample)

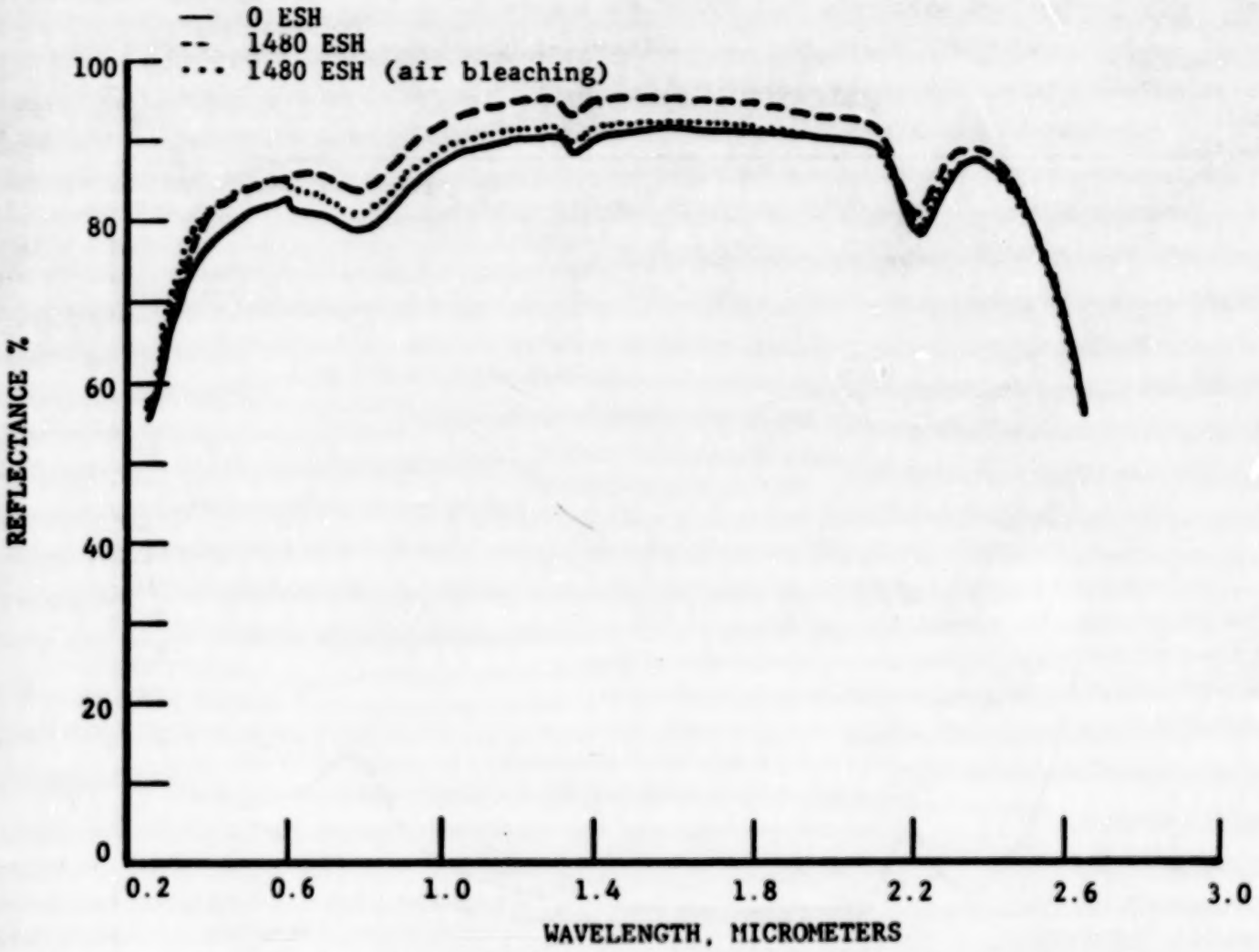

Fig. A-7 Effect of UV Irradiation on the Reflectance of Polyethylene Oxide (2nd sample)

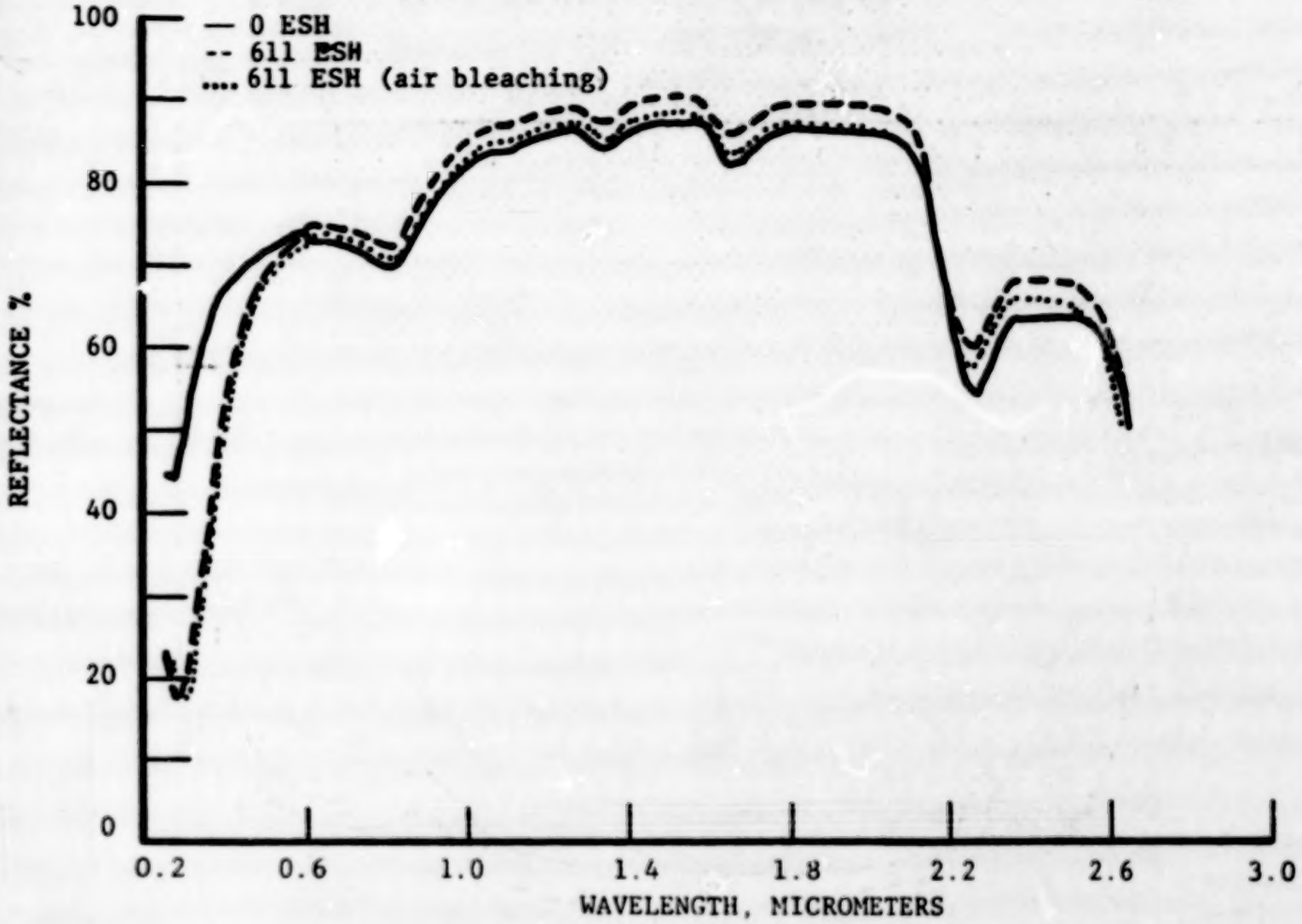

Fig. A-8 Effect of UV Irradiation on the Reflectance of Polytrimethylethylene Oxide

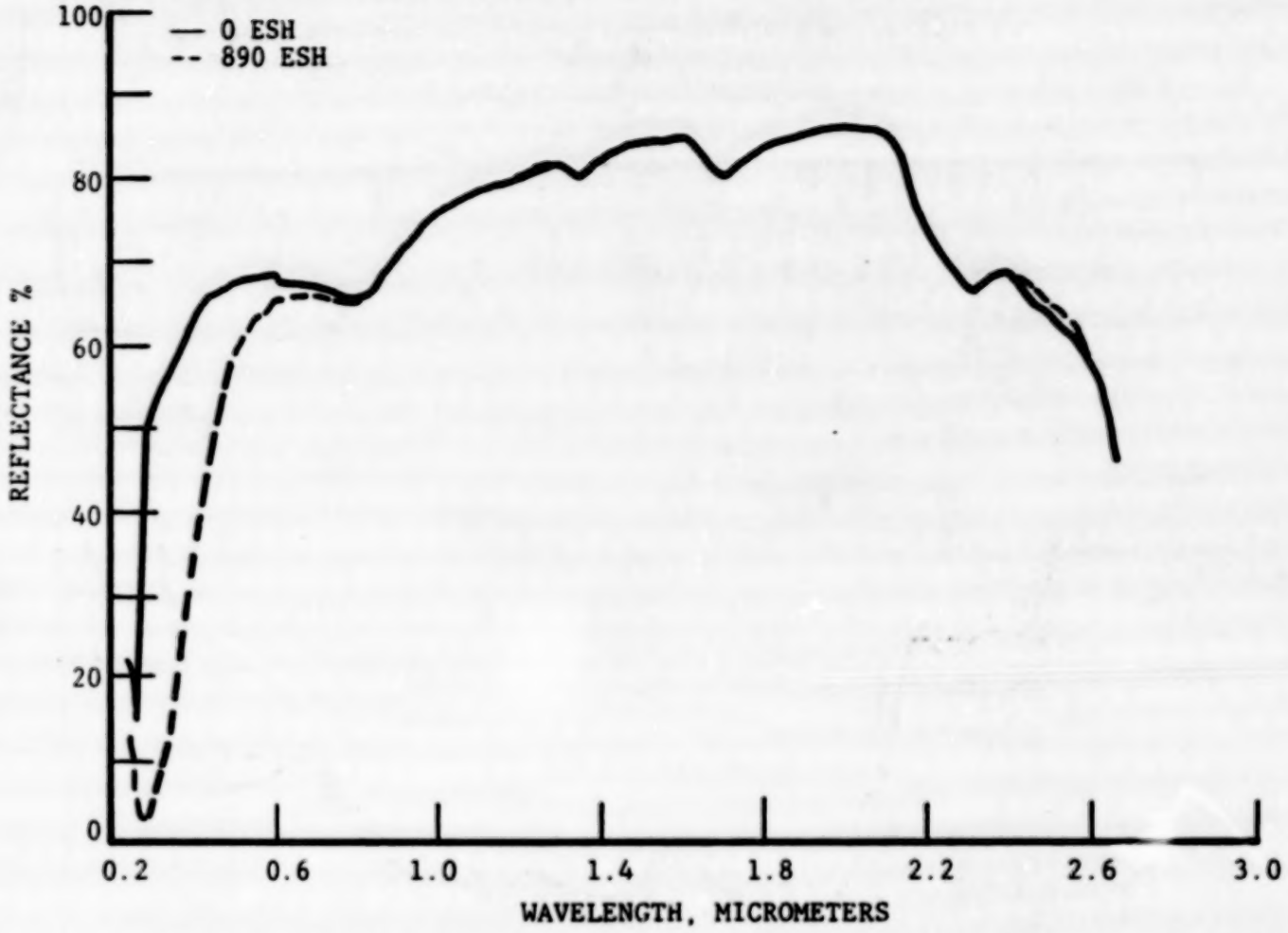

Fig. A-9 Effect of UV Irradiation on the Reflectance of Polycyclohexene Oxide (1st sample)

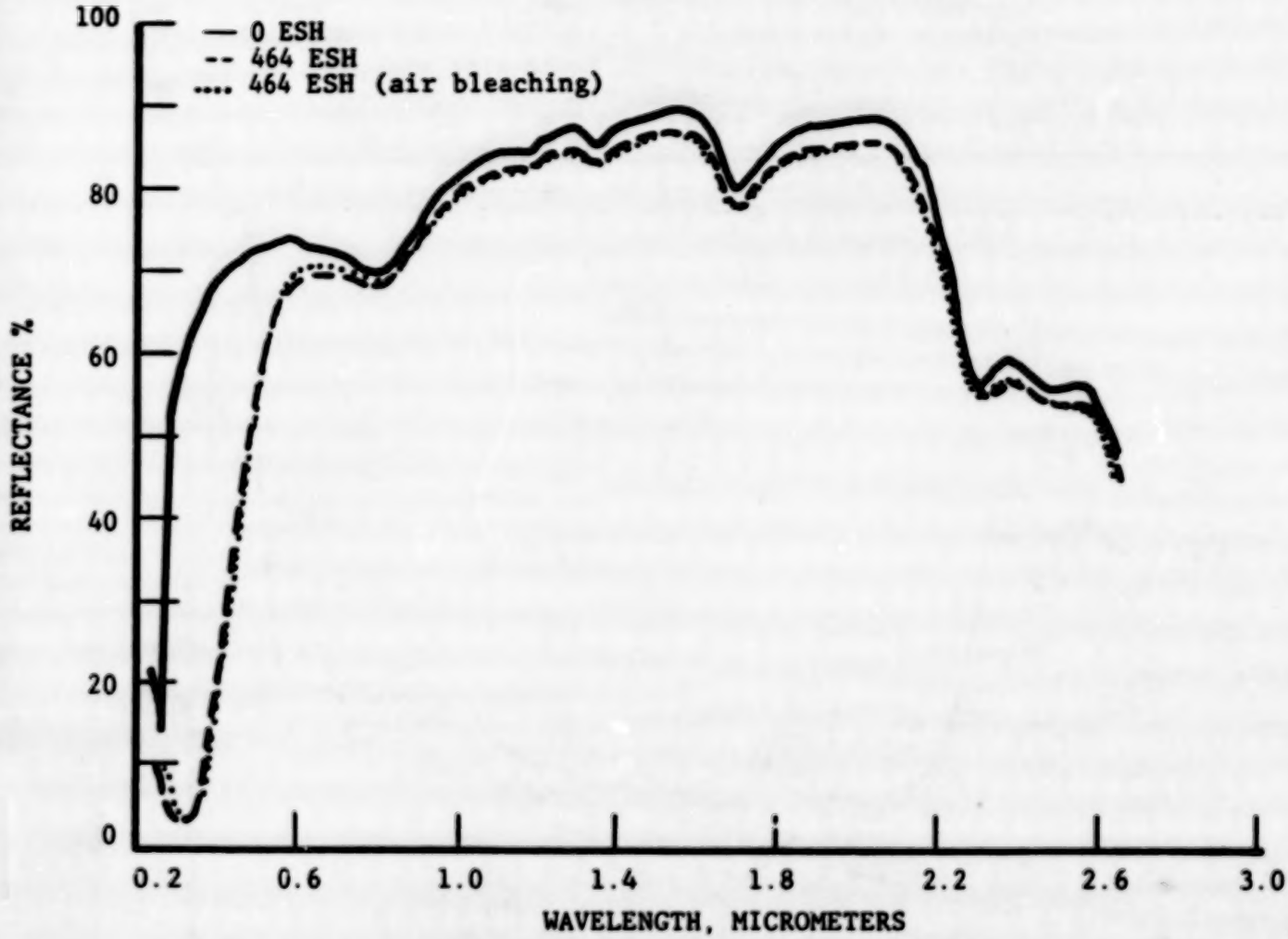

Fig. A-10 Effect of UV Irradiation on the Reflectance of Polycyclohexene Oxide (2nd sample)

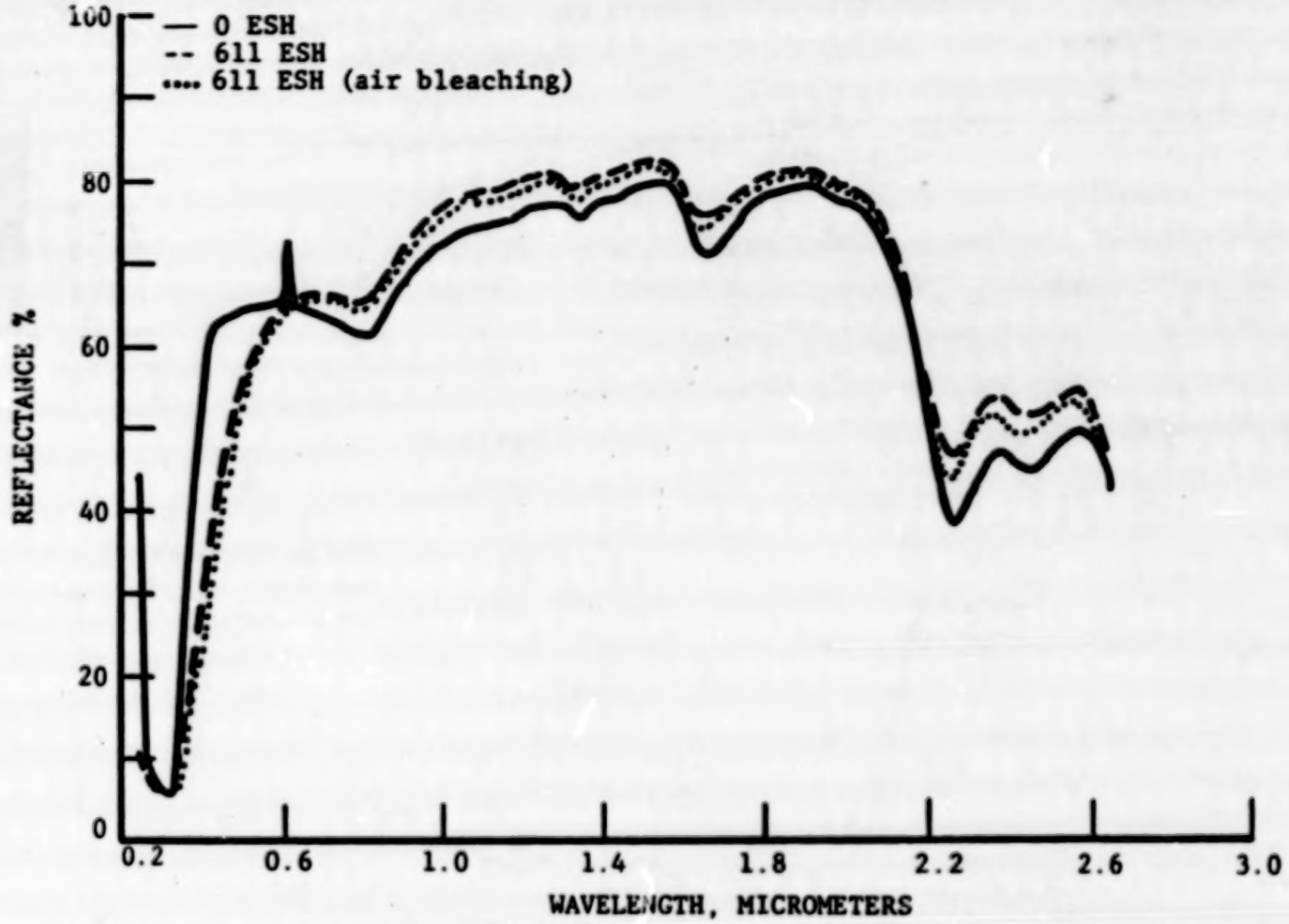

Fig. A-11 Effect of UV Irradiation on the Reflectance of Benzoguanamine/Formaldehyde Resin

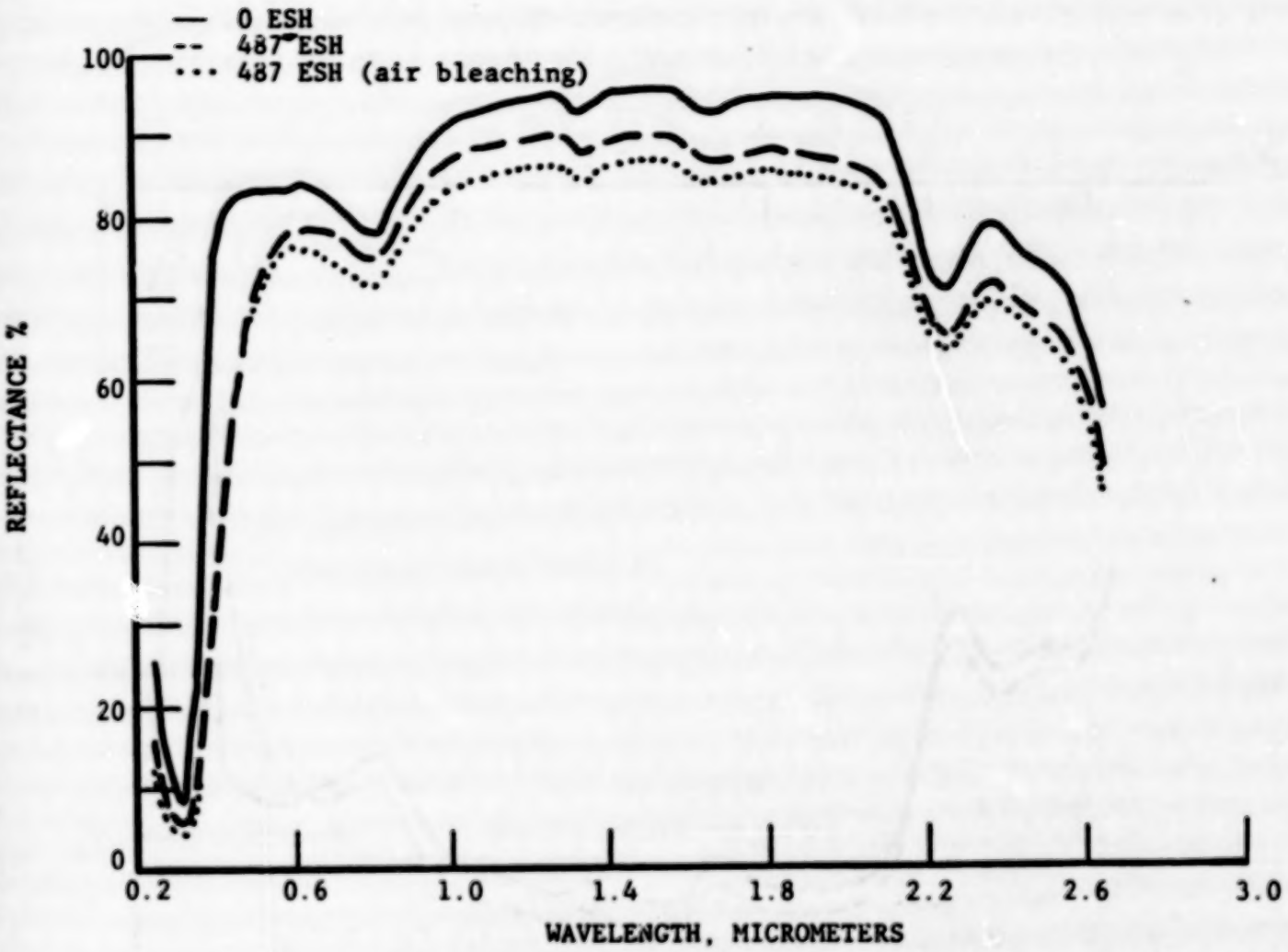

Fig. A-12 Effect of UV Irradiation on the Reflectance of the Copolymer of Benzoguanamine/o-Hydroxybenzoguanamine (98/2) with Formaldehyde

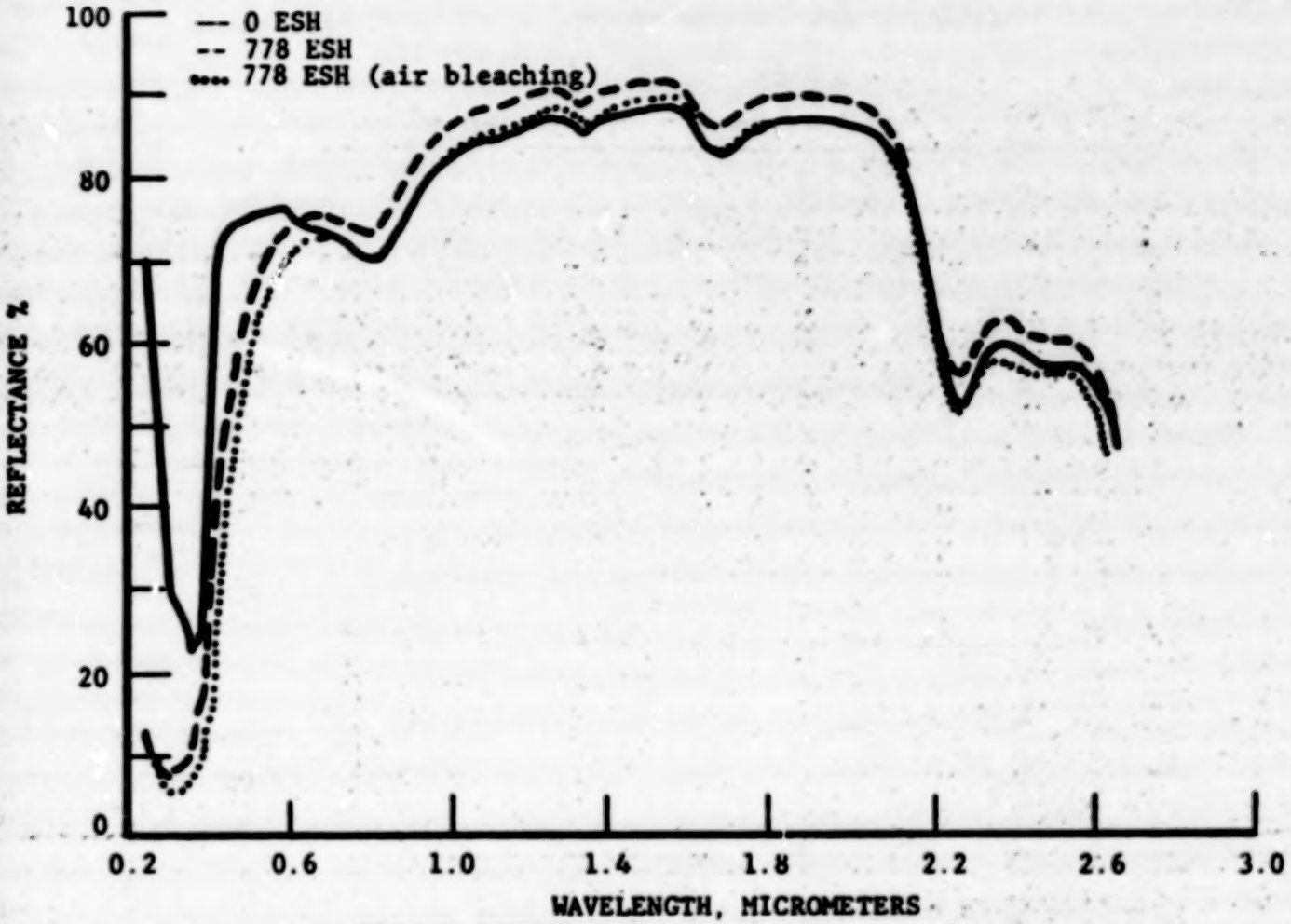

Fig. A-13 Effect of UV Irradiation on the Reflectance of the Copolymer of Benzoguanamine/o-Hydroxybenzoguanamine (50/50) with Formaldehyde

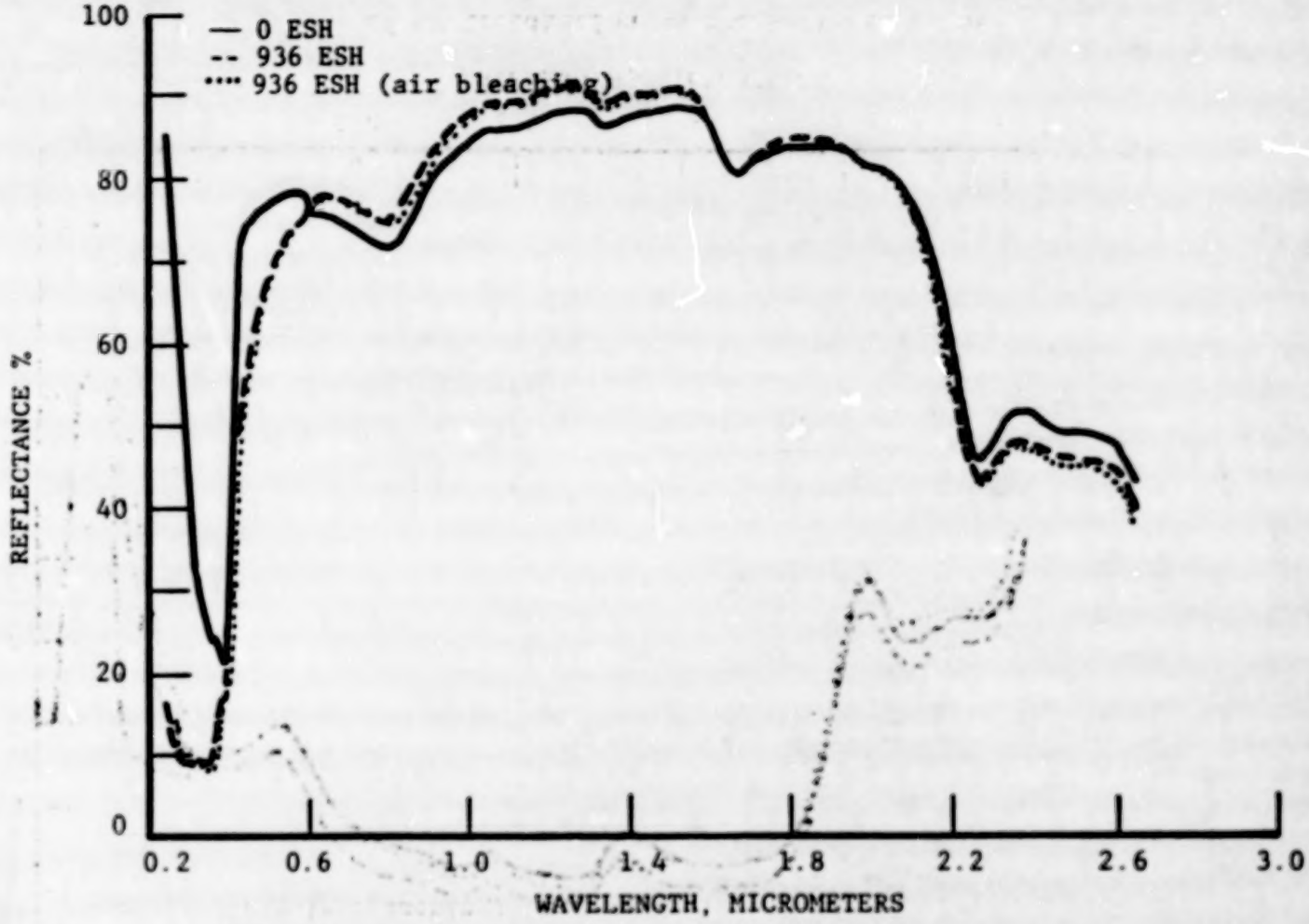

Fig. A-14 Effect of UV Irradiation on the Reflectance of o-Hydroxybenzoguanamine/Formaldehyde Resin

Table A-1

POLYPIVALOLACTONE

Run No.	ESH	α_s	$\Delta\alpha_s$
948	air 0	.209	
341	air 0	.230	
342	vac 0	.244	
343	43	.272	+0.028
344	112	.270	+0.026
345	158	.275	+0.031
346	444	.291	+0.047
347	658	.296	+0.052
348	800	.307	+0.063

Table A-2

POLYCARBONATE FROM NEOPENTYLGLYCOL

Run No.	ESH	α_s	$\Delta\alpha_s$
925	air 0	.224	
301	air 0	.289	
302	vac 0	.282	
303	41	.278	-0.004
304	111	.305	+0.023
305	158	.324	+0.042
307	441	.381	+0.099
381	794	.411	+0.129
383	1126	.419	+0.137
385	1481	.430	+0.148

Table A-3

POLYVINYLCARBAZOLE (FIRST SAMPLE)

Run No.	ESH	α_s	$\Delta\alpha_s$
926	air 0	.223	
291	air 0	.254	
292	vac 0	.252	
293	41	.242	-0.010
294	111	.271	+0.019
296	299	.270	+0.018
297	441	.285	+0.033
298	534	.305	+0.053
371	794	.327	+0.075
373	1126	.339	+0.087
375	1481	.343	+0.091

Table A-4

POLYVINYLCARBAZOLE (SECOND SAMPLE)

Run No.	ESH	α_s	$\Delta\alpha_s$
451 (A)	air 0	.253	
451 (B)	vac 0	.253	
453	41	.252	-0.001
454	112	.257	+0.004
457	609	.264	+0.011
459	1040	.265	+0.012
541	1206	.280	+0.027
543	1538	.286	+0.033
546	1867	.301	+0.048
547	1894	.304	+0.051
548	air 1895	.297	+0.044

Table A-5

POLYVINYLNAPHTHALENE

Run No.	ESH	α_s	$\Delta\alpha_s$
351	air 0	.187	
352	vac 0	.194	
354	112	.202	+0.008
357	658	.212	+0.018
359	965	.217	+0.023
441	1107	.224	+0.030
443	1463	.224	+0.030
444	1485	.226	+0.032

Table A-6

POLYETHYLENE OXIDE (FIRST SAMPLE)

Run No.	ESH	α_s	$\Delta\alpha_s$
927	air 0	.176	
311	air 0	.186	
312	vac 0	.181	
313	41	.179	-0.002
314	111	.168	-0.013
315	158	.165	-0.016
316	299	.157	-0.024
318	534	.161	-0.020
361	794	.157	-0.024
363	1126	.154	-0.027
365	1481	.156	-0.025

Table A-7

POLYETHYLENE OXIDE (SECOND SAMPLE)

Run No.	ESH	α_s	$\Delta\alpha_s$
956	Air Out of Qtz. Tube	.172	
411	air 0	.174	
412	vac 0	.180	
413	42	.162	-0.018
414	112	.159	-0.021
417	608	.151	-0.029
481	1105	.151	-0.029
484	1603	.139	-0.041
486	1934	.135	-0.045
487	1946	.138	-0.042
488	air 1946	.157	-0.023

Table A-8

POLYTHRIMETHYLETHYLENE OXIDE

Run No.	ESH	α_s	$\Delta\alpha_s$
691	air 0	.263	
692	vac 0	.260	
693	48	.269	+0.009
695	277	.268	+0.008
697	539	.277	+0.017
698	611	.279	+0.019
699	air 611	.280	+0.020

Table A-9

POLY(CYCLOHEXENEOXIDE) (1ST SAMPLE)

Run No.		ESH	α_s	$\Delta\alpha_s$
531	air	0	.296	
532	vac	0	.302	
533		42	.304	+0.002
534		112	.308	+0.006
536		278	.329	+0.027
537		444	.339	+0.037
539		775	.349	+0.047
571		815	.369	+0.067
572		890	.372	+0.070

Table A-10

POLY(CYCLOHEXENEOXIDE)
(2ND SAMPLE)

Run No.		ESH	α_s	$\Delta\alpha_s$
671	air	0	.265	
672	vac	0	.253	
673		18	.275	+0.022
674		112	.320	+0.067
676		348	.352	+0.099
678		464	.367	+0.114
679	air	464	.355	+0.102

Table A-11

BENZOGUANAMINE-FORMALDEHYDE RESIN

Run No.		ESH	α_s	$\Delta\alpha_s$
701	air	0	.369	
702	vac	0	.372	.0
703		42	.397	+0.025
705		278	.414	+0.042
707		539	.418	+0.046
708		611	.417	+0.045
709	air	611	.403	+0.031

Table A-12

COPOLYMER OF BENZOGUANAMINE/O-HYDROXYBENZOGUANAMINE (98/2) WITH FORMALDEHYDE

Run No.		ESH	α_s	$\Delta\alpha_s$
661	air	0	.217	
662	vac	0	.196	
663		23	.229	+0.033
665		135	.268	+0.072
666		277	.282	+0.086
669		.487	.288	+0.092
573	air	487	.311	+0.115

Table A-13

COPOLYMER OF BENZOGUANAMINE/O-HYDROXYBENZOGUANAMINE (50/50) WITH FORMALDEHYDE

Run No.	ESH	α_s	$\Delta\alpha_s$
681	air 0	.279	
682	vac 0	.278	
683	43	.298	+0.020
684	138	.304	+0.026
686	445	.303	+0.025
688	706	.319	+0.041
689	778	.321	+0.043
786	air 778	.326	+0.048

Table A-14

O-HYDROXYBENZOGUANAMINE-FORMALDEHYDE RESIN

Run No.	ESH	α_s	$\Delta\alpha_s$
631	air 0	.273	
632	vac 0	.271	
634	88	.284	+0.013
636	275	.282	+0.011
637	417	.291	+0.020
639	747	.304	+0.033
742	936	.302	+0.031
743	air 936	.302	+0.031

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16. Abstract

A literature search in the field of ultraviolet and charged particle irradiation of polymers has been utilized in an experimental program aimed at the development of radiation stable materials for space applications. This report describes the rationale utilized for material selection and the synthesis, characterization and testing performed on several selected materials. Among the materials tested for ultraviolet stability in vacuum, polyethyleneoxide, polyvinylnaphthalene, and the amino resin synthesized by the condensation of o-hydroxybenzoguanamine with formaldehyde have shown promising properties. Particularly interesting, and unexpected, was the radiation behavior of poly(ethyleneoxide), in that irradiation did not cause degradation of optical properties but rather an improvement in transparency as indicated by a decrease in solar absorptance with increasing exposure time. A summary of a literature search in the field of radiation effects and a review of preliminary irradiation tests performed under previous contracts No. NAS1-12549 and No. NAS1-13292 (July 1973 through September 1975) are included for reference.

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